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LXXI. *On a new Method for the Measurement of the Thermal Conductivity of poor and medium Heat-conducting Materials.* By R. W. B. STEPHENS, B.Sc., Imperial College of Science and Technology *.

Introduction.

IN recent determinations of the thermal conductivity of solid insulators the method of electrical heating has been adopted, and usually specimens of comparatively small dimensions have been employed. This limitation of the size of the specimen is disadvantageous when dealing with materials which are non-homogeneous in character, since a small sample may not be truly representative of the bulk of the material. The calorimetric method to be described in this paper enables large specimens to be used without, however, incurring the disadvantage of prolonging the time necessary for the completion of the experimental observations. The essential experimental procedure of this variable state method involves the observation of the rate of rise, or fall, of the temperature of a mass of liquid, contained in a cylindrical tube of the substance under investigation. The tube is immersed in a liquid bath, which is maintained at a suitable temperature.

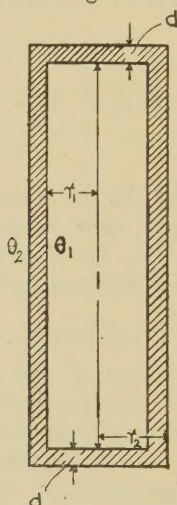
* Communicated by Prof. H. S. Gregory, Ph.D.

Theory of the Method.

Consider the ideal case of a cylindrical tube of the material closed at each end and containing a known mass of liquid (fig. 1).

Let r_1 and r_2 be the internal and external radii respectively of the cylindrical portion of the tube, whose length is l , and let d be the thickness of each of the flat end plates. The outside surface of the tube is maintained at a constant temperature θ_2 , and suppose θ_1 (which is greater than θ_2) to be the temperature of the inside

Fig. 1.



surface at any time t . The liquid contents of the tube are assumed to be efficiently stirred, so that the temperature is sensibly uniform throughout its mass.

Consider unit length of an infinite cylinder (fig. 2) and the thermal equilibrium of an annulus at radius r at any time t . The equation of heat conduction for this annulus is as follows :—

$$2\pi \cdot rK \cdot \frac{d\theta}{dr} = W \cdot \frac{d\theta_1}{dt} + \pi \cdot (r^2 - r_1^2) \cdot c \cdot \frac{d\theta}{dt}, \quad (\text{I.})$$

where K is the thermal conductivity of the material of the tube in cal. cm.⁻¹ sec.⁻¹ deg.⁻¹, c is the thermal capacity per unit volume of the material, W is the thermal

capacity of the liquid contents per unitlength of the tube, and $\bar{\theta}$ is the mean temperature of the material contained between the annulus at r and the inner boundary surface of the tube. The dimensions, temperatures, and time are expressed in cm., degrees Centigrade, and seconds respectively.

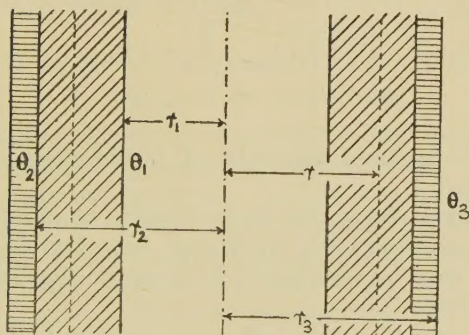
$\bar{\theta}$ will be defined by the following expression :

$$\pi \cdot (r^2 - r_1^2) \cdot \bar{\theta} = \int_{r_1}^r 2\pi \cdot r \cdot dr \cdot \theta, \quad \text{. . . (II.)}$$

where θ is assumed to be given by the steady state distribution, *i. e.*,

$$\theta = \frac{\theta_1 \log_e r/r_2 - \theta_2 \log_e r/r_1}{\log_e r_1/r_2} \quad \text{. . . . (III.)}$$

Fig. 2.



Substituting

$$\bar{\theta} = \frac{1}{(r^2 - r_1^2) \cdot \log_e r_1/r_2} \cdot [\{r^2 \cdot \log_e r - r_1^2 \cdot \log_e r_1 + \frac{1}{2}(r_1^2 - r^2)\}(\theta_1 - \theta_2) - \theta_1 \log_e r_2 \cdot (r^2 - r_1^2) + \theta_2 \cdot \log_e r_1 \cdot (r^2 - r_1^2)]. \quad \text{(IV.)}$$

Hence

$$\frac{d\bar{\theta}}{dt} = \frac{1}{(r^2 - r_1^2) \cdot \log_e r_1/r_2} \cdot [r^2 \log_e r - r_1^2 \log_e r_1 + \frac{1}{2}(r_1^2 - r^2) - r^2 \log_e r_2 + r_1^2 \log_e r_2] \cdot \frac{d\theta_1}{dt} \quad \text{. . . (V.)}$$

so that by plotting $\log_e(\theta_1)$ against t a straight line should be obtained. The value of μ_1 may be determined from the slope of this line, and hence also $\frac{d\theta_1}{dt}$ using relation (IX.).

Finally, equation (VII.) may be written

$$K \cdot \left\{ \frac{2\pi \cdot l}{\log_e r_2/r_1} + \frac{\pi \cdot (r_1^2 + r_2^2)}{d} \right\} \\ = \left\{ W' + \left[\frac{(r_2^2 + r_1^2)d}{2} + \frac{l \cdot F}{(\log_e r_2/r_1)^2} \right] \pi \cdot c \right\} \cdot \mu_1, \quad (\text{XI.})$$

where F denotes the expression

$$\left\{ \frac{(r_2^2 - r_1^2)}{2} - r_1^2 \{ \log_e r_2/r_1 + (\log_e r_2/r_1)^2 \} \right\}.$$

Similarly, equation (VI.) may be written

$$K = \frac{\log_e r_2/r_1}{2\pi} \cdot \left\{ W + \frac{\pi \cdot c \cdot F}{(\log_e r_2/r_1)^2} \right\} \cdot \mu_1. \quad (\text{XII.})$$

Design of the Apparatus.

In fulfilling the ideal experimental conditions implied by the simple theory, a careful consideration of the design of the apparatus in certain details was essential. The efficient stirring of the liquid contents of the tube was ensured by the use of a rotating stirrer, the shaft of which passed through a hole in a plug fitted into the upper end of the tube. This arrangement incidentally eliminated the radiation and evaporation losses occurring at the liquid surface in an open tube. By incorporating a resistance thermometer in the stirrer, it was possible to attain a high order of accuracy in temperature measurement along with a reduction of the thermal capacity of the combination. Furthermore, any serious lag in the recording of the temperature of the cooling liquid was minimized by the adoption of platinum thermometry. The problem of maintaining the tube full of liquid was overcome by the introduction of two funnels in the upper plug, the funnels acting as reservoirs for the necessary liquid to compensate for the decrease in volume of the latter. The dimensions of the tube of the test substance were chosen so that the length was as large as possible in comparison with the internal radius, and, in order

to reduce the importance of the thermal capacity of the walls of the tube, the internal radius was made conveniently large for a given wall thickness. In addition, the thermal capacity of the stirrer was designed to be as uniform as possible along its length, so that equation (XII.) could be applied to the experimental results.

Form of the Specimen.

The material under investigation was obtained in the form of a tube approximately 6 cm. internal diameter and 40 cm. long, the wall thickness being of the order of 0.5 to 0.8 cm. A plug (L) of the same material and thickness as that of the cylindrical walls (T) closed the lower end of the tube (shown in section in fig. 3). The plug was furnished with a screw-thread, enabling a water-tight joint to be made, and at the same time permitting of easy removal if desired. In order to preserve symmetry of the form of the specimen, the upper end of the tube was fitted with two plates (A and B) of the test material, and they were designed so that they could be considered as the thermal equivalent of the plug L. The plate A (shown in detail in fig. 4) was provided with a screw-thread which fitted a corresponding thread cut in a recessed portion of the upper part of the outer surface of the tube T. This plate also contained a circular channel *a*, 1.0 cm. wide and 0.5 cm. deep, which permitted of an ice-cold water circulation through the inlet and outlet tubes *t*. The plate B (fig. 5) consisted essentially of a plug (Y) which closely fitted the inside of the tube T, and a disk-like portion which was in close contact with the upper face of A. Three funnels of the test material (E and F in fig. 5) were set in their respective holes in B by means of Chatterton cement. A metal plate (C), in which two narrow brass tubes (*dd*) were inserted, and a ring of brass (D), which formed a reservoir on its upper surface, rested in position upon B. The plates A, B, and C were clamped together, and to the rim *r* of the right limb of the copper U-tube by clamps (H) as indicated in fig. 6. A stream of ice-cold water was maintained through the tubes *d*, which led into the channelled upper surface of B, and was carried away through an exit tube *h* soldered into the ring D.

Fig. 3.

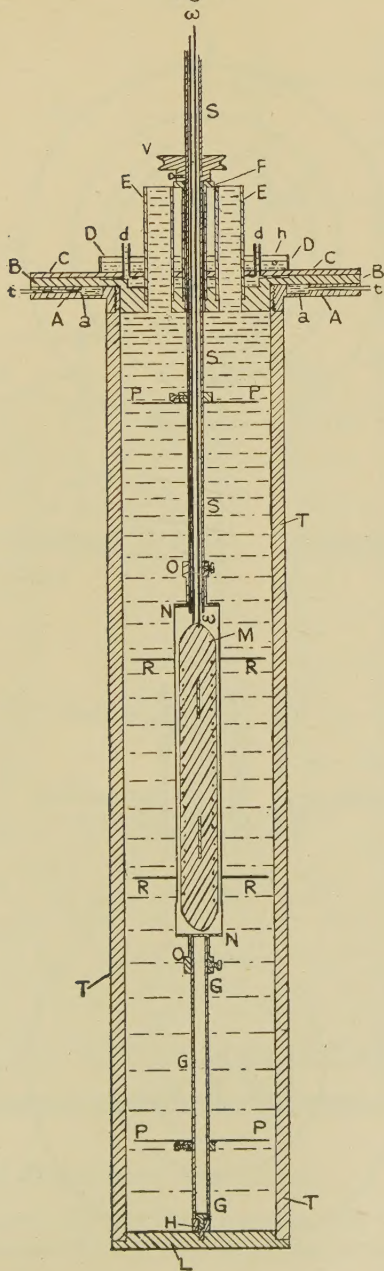


Fig. 4.

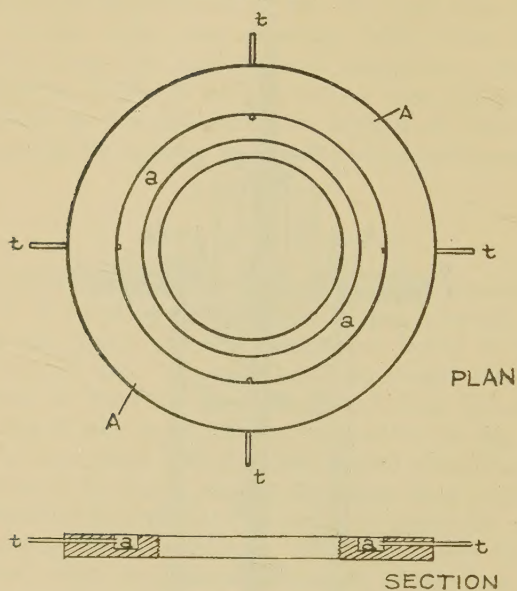


Fig. 5.

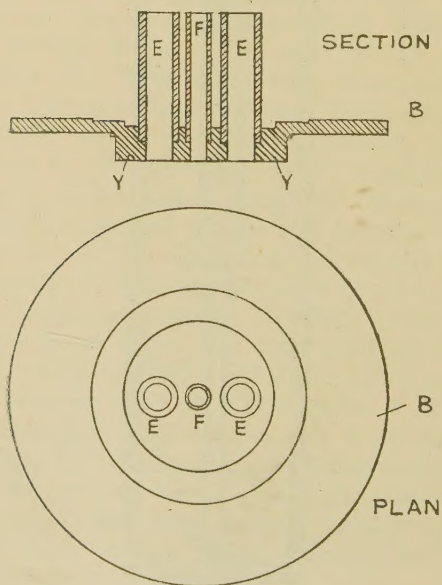
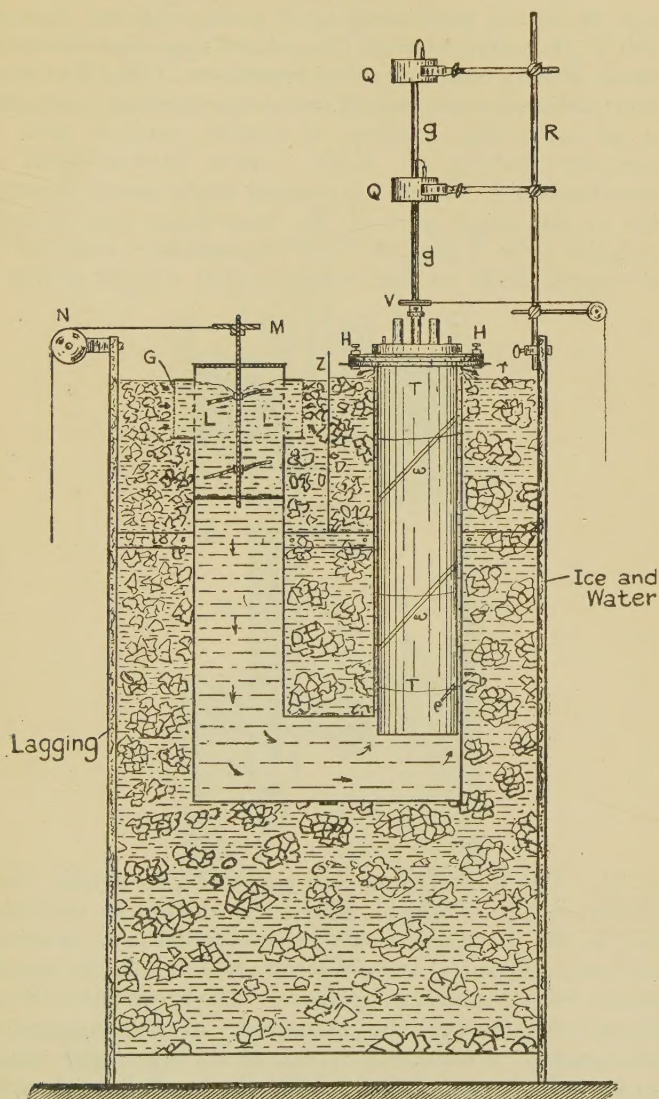


Fig. 6.

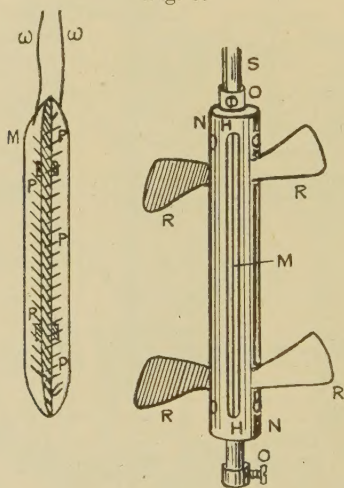


Thermometer and Stirrer.

The temperature of the liquid inside the tube T was measured by means of a combined resistance thermometer

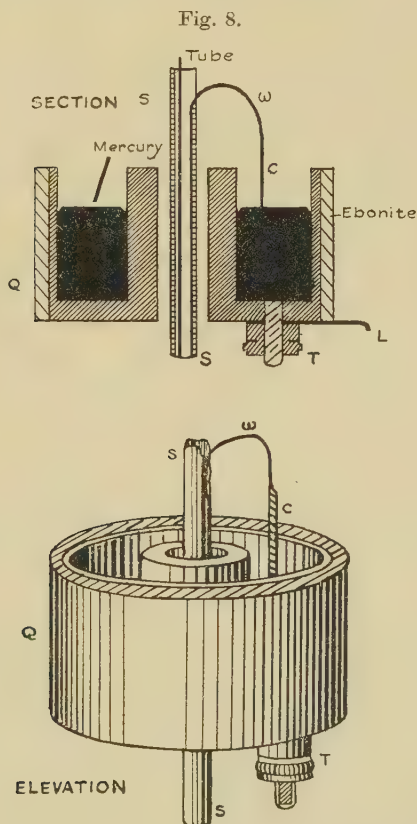
and stirrer. The thermometer consisted of a mica frame, M (fig. 7) perforated by a series of holes through which a platinum wire (4 mils. diam.) *pp* was threaded so as to form a non-inductive resistance. The free ends of the platinum wire, which had been carefully annealed and given a thin coating of shellac varnish with a subsequent baking to $140^{\circ}\text{C}.$, were hard-soldered to copper leads *ww*. These two copper leads passed through holes in the upper part of the mica frame and through a bakelite tube S (figs. 3, 7, and 8), and were soldered at their upper ends to flat amalgamated copper strips, C

Fig. 7.



(fig. 8). The mica frame was contained in a thin brass cylinder, N (figs. 3 and 7), which was slotted as indicated (HH) in fig. 7. Each end of the cylinder was provided with brass collars (O) and set screws which held the similar bakelite tubes S and G in position. The latter tube (G) was utilized to preserve the symmetry of the apparatus, and it carried a water-tight plug at its lower end, which also served as a spindle to work in the small brass bearing H (fig. 3) set into the plug L. The contained liquid was efficiently stirred by the brass blades PP (fig. 3) carried on the bakelite tubes and the blades RR, which were soldered to the cylinder N. The stirrer was rotated by a belt-drive passing round the pulley V (figs. 3 and 6),

which was fixed to the tube S. The lower surface of the pulley worked on a bearing-surface provided by an ebonite cap (shown in fig. 3) fitting on the tube F, which in itself acted as a bearing for the tube S. In order to obtain electrical connexion between the resistance thermo-



meter and the electrical measuring apparatus, the arrangement indicated in fig. 6, and shown in greater detail in fig. 8, was finally adopted. The copper strips soldered to the copper leads dipped into mercury contained in the metal cups Q (figs. 6 and 8), which were electrically insulated from the retort-clamps by a cylinder of ebonite. A Callendar and Griffiths' Bridge was employed to measure the electrical resistance, and leads from this instrument

were connected to brass terminals fixed in the metal cups. It was found by experiment that the mercury attacked the brass cups and ultimately produced a fouling of the electrical contact between the mercury and the metal parts. This trouble was satisfactorily overcome, however, by copper-plating the brass surfaces which were in contact with the mercury.

Wall-thermometer.

This thermometer was used to measure the temperature of the outside surface of the tube T, and consisted of a thin platinum wire wound in intimate contact with this surface. The loop end of this non-inductive winding (*w*) was anchored round a small bakelite peg *p* (fig. 6), and the free ends of the wire were soldered to insulated copper leads which were securely fixed. A thin coating of shellac was applied to the platinum wire, which was held in place at a number of points by thin rubber bands.

The Constant Temperature Bath.

The cooling system consisted essentially of a thin copper U-tube immersed in a bin containing a mixture of ice and water (see fig. 6). Two stirrer-blades were fixed to a shaft which was centrally situated within the left-hand limb of the U-tube, the blades being suitably disposed along the length of the rod to obtain the maximum pumping efficiency. The shaft was motor-driven by means of a belt passing round the pulleys M and N, and the rotation of the blades caused water to be sucked in through the perforations (L) of the walls at the upper end of this limb. The water was then forced up the right limb of the U-tube and over the surface of the ebonite tube T, finally passing out into the bath again through the holes at the upper end (see arrows) of the limb. In order to prevent small pieces of ice from choking the inlet holes (*h*) a wire cage (G), consisting of a cylinder of perforated zinc, encircled the top of the left-hand limb, and, to minimize the possibility of the circulating water passing directly from one limb to the other, a metal sheet (Z) was interposed between them.

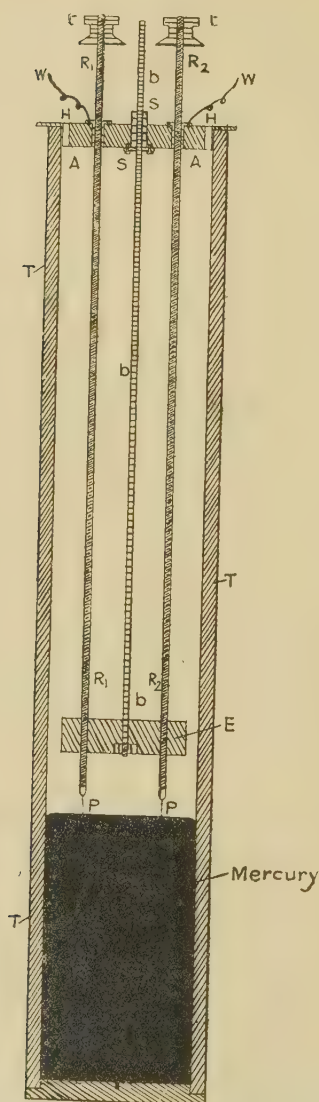
Experimental Procedure.

The ice-bath having been set in circulation for a period of about 30 minutes, distilled water at a temperature of approximately 55°C . was poured into the ebonite tube T until the liquid reached the upper end of the funnels (E and F). The contained water was vigorously stirred, and after a lapse of a few minutes, observations of temperature and time were simultaneously made, at frequent intervals. For this purpose the wire contact of the Callendar and Griffiths' Resistance Bridge was set at pre-determined values, so that, in general, the galvanometer spot was deflected from its previously ascertained zero position on the scale. The magnitude of the resistance in the bridge being less than that corresponding to the existing temperature of the thermometer, the scale deflexion would gradually decrease. On the passage of the spot of light through zero, a key was depressed in the circuit of an electromagnet. This latter operated a pen which formed a suitable trace on the drum of a chronograph; a further relay, actuated by an electric clock, marked a time-base record for the interpretation of the readings. This experimental procedure was repeated over the required temperature range, while at suitable intervening periods the resistance of the wall-thermometer was ascertained in a similar manner.

Calibration of Tubes.

The uniformity of the internal diameter of the ebonite tube T was tested by means of the apparatus shown in fig. 9. R_1 and R_2 are brass screw-threads passing through brass sleeves set in a bakelite plug (A), which closely fits the tube T. The lower extremities of R_1 and R_2 pass through an ebonite block (E) which is fixed to a brass rod (*b*) and acts as a distance piece. A platinum wire (*p*) is soldered to the lower end of each brass screw; sharper contact between the platinum and mercury is obtained if the previously cleaned platinum points are raised to a red heat and plunged a number of times into a paste of mercury-sodium amalgam. To carry out the calibration, assuming T to contain mercury at a suitable level, R_1 and R_2 are adjusted until the platinum points touch the mercury surface. This adjustment is facilitated by

Fig. 9.



connecting a galvanometer and battery in series with the leads *W*, so that the required condition will be realized by the completion of the electric circuit. The heights

of the "reference lines" of the terminal heads t are then taken by means of a cathetometer microscope, and after this measurement the platinum points are raised through a suitable distance. A convenient quantity of mercury, whose volume must be known, is introduced into the tube T *via* the holes H in the plug A, and adjustment is again made for the completion of the electrical circuit. A second cathetometer reading of the heights of the terminal heads will enable the mean internal diameter of the tube over this length to be calculated. In this manner the bore of the ebonite tube may be cali-

Typical Calibration Measurements.

Ebonite Tube "B."

Temperature 15.0°C.

Mass of mercury. added (in gm.).	Rise of mercury in tube (cm.).	Internal radius of tube (cm.).
580.05	1.375	3.147
580.70	1.385	3.137
579.65	1.385	3.135
579.20	1.380	3.139

Mass of salt solution added (in gm.).	Rise of level in tube (cm.).	Internal radius of tube (cm.).
102.1	3.30	3.121
138.0	4.43	3.137
124.0	3.99	3.133

brated over any desired range. Since a large amount of mercury would be required in the calibration of the upper portions of the tube, it is a convenience to substitute the mercury by a dilute aqueous salt solution of known density.

Corrections to Formula.

In the derivation of equation (XII.) it has been tacitly assumed that the temperature of the outside surface of the ebonite tube T corresponded to that of the thermostat bath, and remained invariable with time. The

experimental observations, however, showed this surface to be at a higher temperature than the ice-bath, indicating the existence of a stationary fluid layer in contact with the wall. In accordance with this view, it is necessary to note that the wall-temperature decreased with time, in a manner to be expected from the cooling of the liquid contained in the tube T.

Consider unit length of the cylindrical portion of the tube, a section of which is shown in fig. 2. This diagram also indicates the fluid layer as having internal and external radii r_2 and r_3 respectively, θ_2 and θ_3 being the corresponding temperatures of the boundary surfaces.

Equation (XII.) may now be written as

$$\frac{2\pi}{\log_e r_2/r_1} \cdot K \cdot (\theta_2 - \theta_1) = W \cdot \frac{d\theta_1}{dt} + \frac{\pi \cdot c \cdot F}{(\log_e r_2/r_1)^2} \cdot \frac{d(\theta_1 - \theta_2)}{dt},$$

or

$$K = \frac{M}{(\theta_2 - \theta_1)} \cdot \frac{d\theta_1}{dt} + \frac{N}{(\theta_2 - \theta_1)} \cdot \frac{d(\theta_1 - \theta_2)}{dt}, \quad (\text{XIII.})$$

where M and N are calculated from the constants of the tube.

Now it was deduced from the experimental observations that, within a limited temperature range, the following expressions were valid to the order of accuracy of the experiment :

$$(a) \theta_1 = B \cdot e^{-\mu_1 t}, \quad \text{and} \quad (b) \theta_2 = A \cdot e^{-\mu_2 t}.$$

Hence, by differentiation, we obtain

$$\frac{d\theta_1}{dt} = -\mu_1 \theta_1 \quad \text{and} \quad \frac{d\theta_2}{dt} = -\mu_2 \theta_2.$$

It follows that

$$\begin{aligned} \frac{d(\theta_1 - \theta_2)}{dt} &= \frac{d\theta_1}{dt} - \frac{d\theta_2}{dt} \\ &= \mu_2 \theta_2 - \mu_1 \theta_1. \end{aligned}$$

On substitution, equation (XIII.) becomes

$$K = M \cdot \mu_1 \cdot \left(\frac{\theta_1}{\theta_1 - \theta_2} \right) + \frac{N}{(\theta_1 - \theta_2)} \cdot (\mu_1 \theta_1 - \mu_2 \theta_2)$$

$$\text{or } K = M \cdot \mu_1 \cdot \left(\frac{\theta_1}{\theta_1 - \theta_2} \right) + N \cdot \left\{ (\mu_1 + (\mu_1 - \mu_2) \cdot \left(\frac{\theta_2}{\theta_1 - \theta_2} \right)) \right\} .$$

. . . (XIV.)

Method of Calculation of the Experimental Results.

The thermal conductivity (K) of ebonite has been calculated from the experimental results by the use of equation (XIV.), which refers to the case of an isolated element in an infinite tube. In this instance the equation has been applied to the central portion of the finite tube of the specimen. A theoretical justification of this mode of deduction of the final figures is contained in the mathematical analysis developed in a recent paper by Yosikata*. This writer determines the error involved by the application of the equation of the infinite cylinder, to the calculation of the heat-loss in the finite case. The case considered is that in which the inner surface of the cylinder is at a certain constant higher temperature than that of the outer surface. The percentage error e of the heat-loss in the middle section of the inner surface of the finite cylinder, compared with that of the infinite cylinder, is defined by

$$e = \left\{ \frac{\int_{l_1}^{l_2} \left(\frac{d\theta}{dr} \right)_{r=r_1} \cdot dz - \left(\frac{d\theta}{dr} \right)_{r=r_1} \cdot l}{\left(\frac{d\theta}{dr} \right)_{r=r_1} \cdot l} \right\} \times 100,$$

where l denotes the total internal length of the finite tube under test (see fig. 10) and ABCD represents the portion of the tube in which the heat-loss is compared with that of a similar length of an infinite tube. In the present experiments the approximate dimensions are given by $l=41$ cm. ($l_2-l_1/l=0.5$, $r_1=3.1$ cm., and $r_2=3.8$ cm. An estimation of the error e for cylinders of these dimensions indicates that it is less than 0.5 per cent., *i. e.*, less than the accuracy of the method.

Experimental Data.

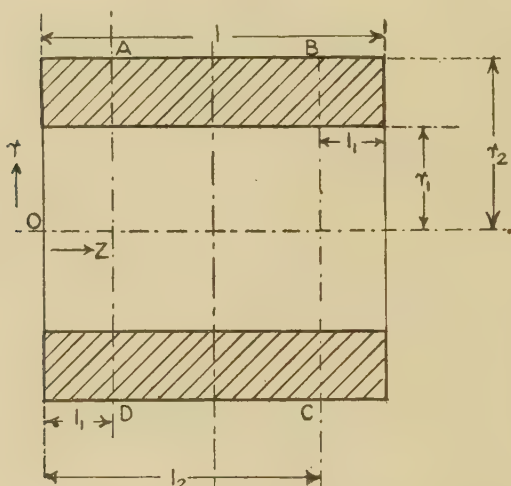
Stirrer Thermometer :—

Resistance at 0 deg. C.	1457.12 cm. bridge wire units.
Fundamental interval	467.44 " " "

* Technology Reports, Tohoku Imperial University, vol. ix. no. 3 (1930).
Phil. Mag. S. 7. Vol. 15. No. 101. May 1933. 3 M

Thermal capacity of thermometer over central 18.30 cm.	= 6.0 cal. per deg. C.
Volume of thermometer over central 18.30 cm.	= 13.2 c.c.
Total thermal capacity of contents of central 18.30 cm. of ebonite tube "A" at t deg. C.	= $547.5s + 6.0$ cal. per deg. C.
Total thermal capacity of contents of central 18.30 cm. of ebonite tube "B" at t deg. C.	= $568.3s + 6.0$ cal. per deg. C., where s is the thermal capacity of water in calories per c.c. at t deg. C.

Fig. 10.



The thermometer was designed so that over the central portions of each ebonite tube the thermal capacity of the contents was constant, as indicated by the following figures :—

Tube "A" :—

Length of tube considered (cm.)	18.30	21.30	23.30	25.30
Thermal capacity per cm. length at 20° C. (calories per deg. C.)	30.19	30.20	30.21	30.22

Tube "B" :—

Length of tube considered (cm.)	18.30	21.30	23.30	25.30
Thermal capacity per cm. length at 20° C. (calories per deg. C.)	30.60	30.61	30.61	30.62

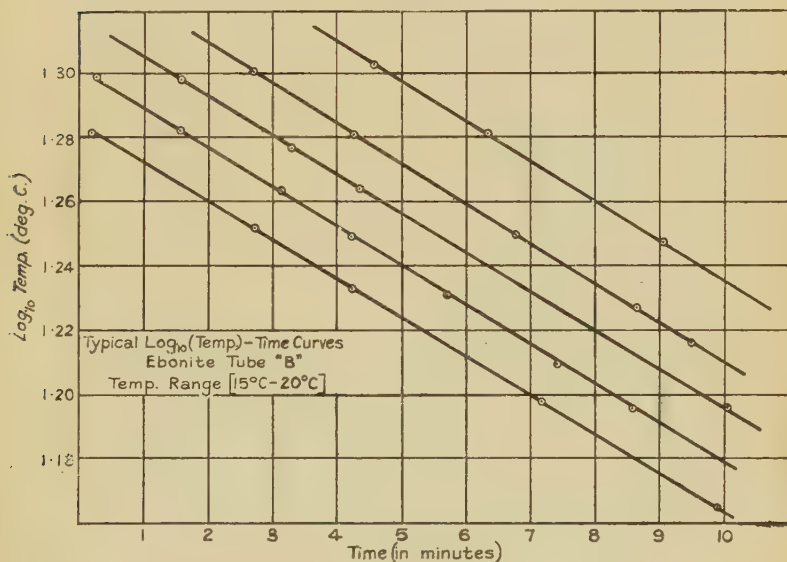
Mean radii of tubes over central portions :—

Tube "A"	$r_1 = 3.123$ cm.	$r_2 = 3.856$ cm.
Tube "B"	$r_1 = 3.139$ cm.	$r_2 = 3.705$ cm.

Calculation of μ_1 and μ_2 .

A series of straight lines were drawn showing the relation between $\log \theta_1$ and time for temperature intervals of approximately 5°C . A typical set of curves is shown in fig. 11. The values of μ_1 calculated from the slopes of these lines are tabulated below, the value of μ_1 for any particular temperature range being the mean of five or more slopes.

Fig. 11.



Tube "A" :—

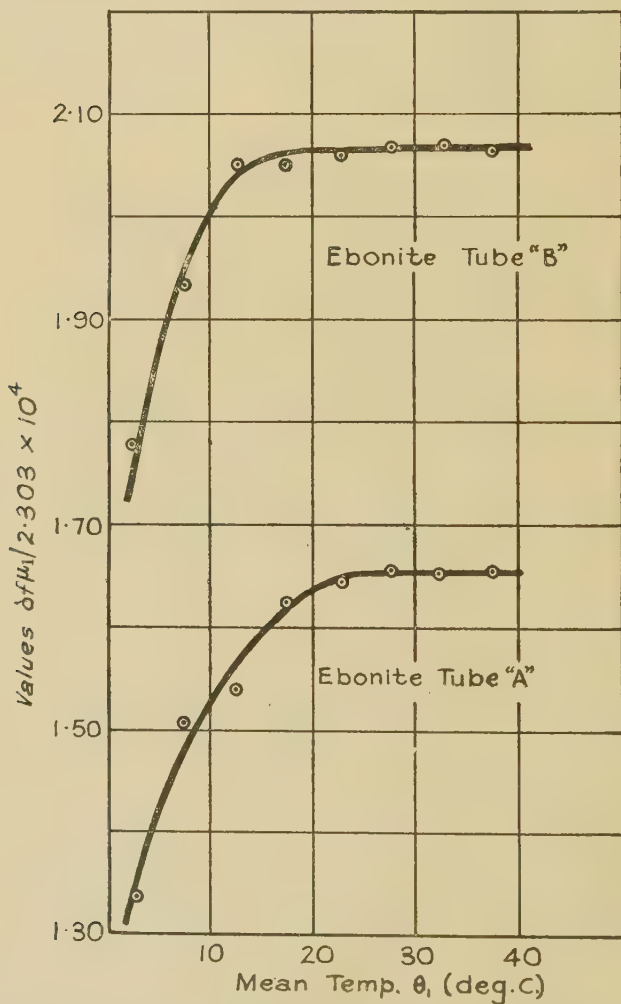
$\mu_1 \times 10^4$	1.507	1.540	1.624	1.647	1.659	1.650	1.656
2.3026							
Mean θ_1 ($^\circ \text{C.}$)	7.5	12.5	17.5	22.5	27.5	32.5	37.5

Tube "B" :—

$\mu_1 \times 10^4$	1.772	1.931	2.051	2.049	2.060	2.068	2.070	2.064
2.3026	...							
Mean θ_1 ($^\circ \text{C.}$)	4.2	7.5	12.5	17.5	22.5	27.5	32.5	37.5

The above values of μ_1 were plotted against the mean θ_1 of each temperature interval. It is evident from the resulting curves (fig. 12) that over a temperature range

Fig. 12.



from 25° C. to 40° C., the value of μ_1 is practically constant. This result indicates that it is permissible to apply the theory of the experiment to the readings pertaining to this temperature range.

Tube "A" :—

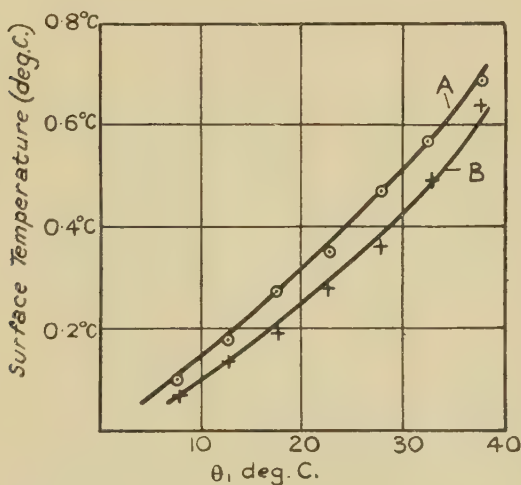
$$\frac{\mu_1}{2.3026} = 1.657 \times 10^{-4} \text{ over the range } 25^\circ \text{ C. to } 40^\circ \text{ C.}$$

Tube "B" :—

$$\frac{\mu_1}{2.3026} = 2.067 \times 10^{-4} \text{ over the range } 25^\circ \text{ C. to } 40^\circ \text{ C.}$$

The values of μ_2 were found by plotting $\log \theta_2$ against time, and hence determining the slopes of the straight lines which were obtained.

Fig. 13.



Tube "A" :

$$\frac{\mu_2}{2.3026} = 1.48 \times 10^{-4};$$

Tube "B" :

$$\frac{\mu_2}{2.3026} = 3.52 \times 10^{-4}.$$

Fig. 13 shows the relation between the outer surface temperature θ_2 and the temperature θ_1 of the contents of the tube. This relation is utilized in the calculation of K from equation (XIV.).

Calculation of the Thermal Conductivity (K.).

Using equation (XIV.) the following values of K are calculated from the experimental results.

Tube.	Mean temp. (°C.).	K (cal. cm. ⁻¹ /sec. ⁻¹ /deg. ⁻¹)
A	14.0	0.000415
A	19.1	0.000413
B	14.0	0.000415
B	19.1	0.000415

The specific heat of the ebonite was found by separate experiment to be 0.33 cal./gm. per deg. C. and the density 1.219 gm. per c.c. at 12° C. (coefficient of cubical expansion = 0.00028 per deg. C.). It is to be noted that the term involving the thermal capacity of the walls of the tube formed only about 6 per cent. of the total thermal capacity of the tube and its contents. The possibility of absorption of moisture by the specimen was tested by weighing the tube before and after immersion in the ice-bath. No appreciable change was recorded.

An estimation of the effective thickness ($r_3 - r_2$) of the stationary liquid layer in contact with the outer surface of the ebonite tube.

If we refer once again to fig. 2, and consider the thermal equilibrium both of the isolated element of the tube and of the superincumbent liquid layer, then we may write

$$\frac{2\pi \cdot K}{\log_e r_2/r_1} (\theta_1 - \theta_2) = \frac{2\pi \cdot K_w}{\log_e r_3/r_2} (\theta_2 - \theta_3),$$

where K_w is the thermal conductivity of water at 0° C. in cal. cm.⁻¹/sec.⁻¹/deg.⁻¹, and the remaining symbols have the meaning previously associated with them.

Hence it follows that

$$\log_e r_3 - \log_e r_2 = \frac{K_w}{K} \cdot \log_e r_2/r_1 \cdot \left(\frac{\theta_2 - \theta_3}{\theta_1 - \theta_2} \right). \quad (\text{XV.})$$

Now the thermal conductivity of ebonite may be considered constant over the temperature range investigated, and since the mean temperature of the liquid layer will never differ by as much as 1° C. from the bath temperature (in this case 0° C.), we deduce from equation (XV.) that $\left(\frac{\theta_2 - \theta_3}{\theta_1 - \theta_2}\right)$ should be approximately constant.

Experimental Data.

Ebonite Tube "A":

$\theta_1(^{\circ}\text{C.})$	17.50	22.50	27.50	32.0
$\left(\frac{\theta_2 - \theta_3}{\theta_1 - \theta_2}\right)$	0.0160	0.0169	0.0173	0.0177

Mean value of $\left(\frac{\theta_2 - \theta_3}{\theta_1 - \theta_2}\right) = 0.170$.

Hence, assuming K for water at 0° C. to be 0.00145 cal., cm.⁻¹/sec.⁻¹/deg.⁻¹, we obtain $r_3 = 3.905$ cm., and therefore $r_3 - r_2 = 0.049$ cm.

The mean value of $\left(\frac{\theta_2 - \theta_3}{\theta_1 - \theta_2}\right)$ deduced from readings obtained with Tube B was 0.0153 , giving $r_3 - r_2 = 0.038$ cm.

Conclusion.

A method has been developed for the rapid determination of the thermal conductivity of medium or poor conductors. The concordance of the final experimental results for different size tubes indicates that the theoretical treatment of the method satisfies the experimental conditions. It should be noted, however, that due consideration must be given to the choice of the salient dimensions of the specimen. The value of the thermal conductivity of ebonite at room temperature as determined by the present method, shows good agreement with the results of the classical investigations of Lees and the more recent work of Griffiths and Kaye. Lees *, using a plate of ebonite (thickness 0.130 cm.), found the thermal conductivity at 35° C. to be 0.00042 cal. cm.⁻¹/sec.⁻¹/

* Phil. Trans. exci. p. 399 (1898).

deg.⁻¹. Griffiths and Kaye * also adopted a modification of the plate method and found the thermal conductivity to vary between the values 0.00038 to 0.00044 cal. cm.⁻¹/sec.⁻¹/deg.⁻¹ at 25° C. for various samples of ebonite. The thickness of their specimens varied from 0.035 cm. to 0.15 cm. The final value of the thermal conductivity of ebonite (density 1.22 gm. per c.c. at 12° C.), as derived from the present experiments, is 0.00041₅ cal. cm.⁻¹/sec.⁻¹/deg.⁻¹ at a mean temperature of 17° C.

As previously mentioned, the present method permits of easy assemblage of the apparatus and enables the thermal conductivity of an insulating material to be rapidly determined, if the substance can be readily obtained in the cylindrical form. It should be emphasised, however, that smaller tubes may be utilized and mercury thermometry adopted, without unduly increasing the experimental errors. In point of fact, the method has been used in this manner, as a laboratory experiment for a considerable period, and consistent values of the thermal conductivity, to within 2 or 3 per cent., have been readily obtained. In this case the outer surface of the tube (approximately 20 cm. long, 3.5 cm. internal diameter, and 0.4 cm. wall thickness) has been cooled by a constant water circulation through a suitable jacket.

If we refer again to equation (XII.), it would appear that by using two or more liquids of known specific heat to "calibrate the tube" the experiment may be adapted to the determination of the specific heat of liquids. Furthermore, if the wall thickness is made larger in comparison with the internal diameter, than is the case of the present experiments, then the thermal capacity of the material of the tube will become of greater importance. Hence the application of equation (XII.) to tubes of these new dimensions should enable the specific heat of the substance to be measured. It is proposed to deal with these additional aspects of the method in future communications.

In conclusion, the author desires to acknowledge his indebtedness to Dr. H. S. Gregory for his kind and helpful interest in the research, also to Mr. C. Hillary and the workshop staff for their care in the construction of the apparatus.

* Proc. Roy. Soc. ser. A, civ. (1923).

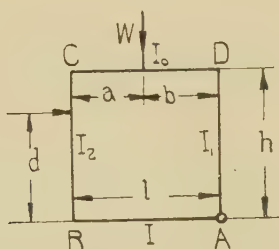
LXXII. *The Experimental Determination of the Forces and Moments in the Elements of Statically Indeterminate Structures.* By Prof. F. C. LEA, D.Sc.*

THE degree of indeterminateness of a structure can readily be obtained from the general formula

$$N - 3S = D,$$

N being the number of degrees of constraint at all the joints and at the fixings to the ground, S the number of members, and D the degree of indeterminateness. For example, a square frame (fig. 1) with rigid joints, pinned to the ground at the point A, supported at B, and loaded in any manner, has three degrees of indeterminateness, or three

Fig. 1.



independent elastic equations are required for its solution. To fix the frame to the ground one degree of constraint is required at B and two at A. Since the joints are rigid, there are three degrees of constraint at each joint and N, therefore, equals $12 + 3 = 15$. Then $D = 15 - 12 = 3$.

There are four unknown moments acting at the joints, A, B, C, D, but these are not independent. When all the loads are vertical,

$$M_A + M_B + M_C + M_D = 0,$$

and when a force F is applied on the vertical CB

$$Fd + M_A + M_B + M_C + M_D = 0.$$

At any joint such as A, $M_{AD} + M_{AB} = 0$. A similar expression can be written down for each of the joints.

With the form of structure shown in fig. 2 there are

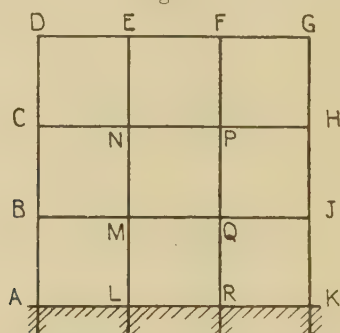
* Communicated by the Author.

three constraints at the base of each column, six at joints similar to B, three at joints such as D, and nine constraints at joints such as Q. There are thus twenty-seven degrees of indeterminateness, and the number of equations required to solve the problem is formidable.

Several elegant methods have been devised for writing down the elastic equations, one derived from Clerk Maxwell's proof that the differential of the total internal work with respect to any load, or Moment, is equal to the displacement of the load, or Moment, in the direction of the load, or Moment. When there is no movement the differential is equal to zero.

Considering the frame A, B, C, D (fig. 1), the work done by direct thrust or tension and shear can be

Fig. 2.



neglected as compared with that done by bending moments. The work done by bending moment is

$$\begin{aligned}
 U = & \int_0^l \left\{ M_{AB} - (M_{AB} - M_{BA}) \frac{x}{l} \right\}^2 \frac{dx}{2EI} \\
 & + \int_0^l \left\{ M_{AD} - (M_{AD} - M_{DA}) \frac{x}{h} \right\}^2 \frac{dx}{EI_1} \\
 & + \int_0^d \left\{ M_{BC} - (M_{BC} - M_{CB}) \frac{x}{l} - \frac{F(h-d)}{l} x \right\}^2 \frac{dx}{2EI_2} \\
 & + \int_0^{h-d} \left\{ M_{CB} - (M_{CB} - M_{BC}) \frac{x}{l} - \frac{Fdx}{l} \right\}^2 \frac{dx}{2EI_2} \\
 & + \int_0^a \left\{ M_{CD} - (M_{CD} - M_{DC}) \frac{x}{l} - \frac{Wbx}{l} \right\}^2 \frac{dx}{2EI_0} \\
 & + \int_0^b \left\{ M_{DC} - (M_{DC} - M_{CD}) \frac{x}{l} - \frac{Wax}{l} \right\}^2 \frac{dx}{2EI_0},
 \end{aligned}$$

the second-moments of the areas of the respective sections of the elements being as shown on fig. 1, and x defines the position of a section from one end of the element. Then

$$\frac{\partial U}{\partial M_{AB}} = 0, \quad \frac{\partial U}{\partial M_{CA}} = 0, \quad \frac{\partial U}{\partial M_{CL}} = 0.$$

Again,

$$M_{CD} + M_{CB} = 0,$$

$$M_{DC} + M_{DA} = 0,$$

$$M_{AB} + M_{AD} = 0,$$

$$M_{BA} + M_{BC} = 0,$$

and since F is the only horizontal force

$$Fd + M_{BC} + M_{AB} + M_{CD} + M_{DC} = 0.$$

Eight equations for the eight unknown moments, or in reality for the four unknowns acting at the four joints.

Maxwell's Theorem of Reciprocal Displacement.

Maxwell's theorem of reciprocal displacements, which states that the displacement produced at any point A of an elastic structure, due to unit load B , in the direction of the load at A is equal to the displacement produced at B in the direction of the load at B by unit load at A , is easily proved. The load may be a direct load or a moment.

The most general case is when a load P acts at a point A of an elastic structure and a moment M at B , as, for example, in fig. 5. Let ∂_{aa} be the linear deflexion produced at A in the direction of P by unit load at A . Let ∂_{ab} be the deflexion in the direction of P by unit moment at B . Let ϕ_{bb} and ϕ_{ba} be the angular deflexions at B in the direction of the moment M due to unit moment at B and unit load at A respectively. Then if a load P be applied to the structure the work done is $\frac{1}{2}P^2\partial_{aa}$. If, now, a couple M is applied the work done is

$$\frac{1}{2}M^2\phi_{bb} + MP\partial_{ab},$$

and the total elastic energy is

$$U = \frac{1}{2}M^2\phi_{bb} + MP\partial_{ab} + \frac{1}{2}P^2\partial_{aa}.$$

Similarly, if M is now applied first

$$U = \frac{1}{2}M^2\phi_{bb} + \frac{1}{2}P^2\partial_{aa} + PM\phi_{ba},$$

or

$$MP\partial_{ab} = PM\phi_{ba}$$

and

$$\partial_{ab} = \phi_{ba}.$$

If at B there is a load P_1

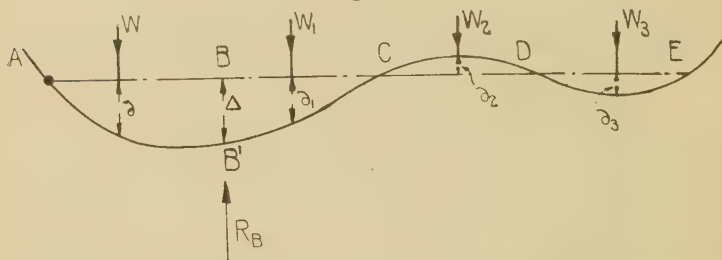
$$\partial_{ab} = \partial_{ba},$$

and if there are moments at A and B

$$\phi_{ab} = \phi_{ba}.$$

By giving any displacement at A and measuring the displacement at B , the "effect" produced at B by a load at A can be determined.

Fig. 3.



As an example the method can be used to determine the reactions of any form of continuous beam.

Let A, B, C, D (fig. 3) be any continuous beam having a variable moment of inertia of section. Let it be required to determine the reactions due to any system of loading. When the reactions are known the bending-moment and shearing-force diagrams can be drawn. Let a model be made of the beam in any suitable material. To determine the reactions at any support such as B displace the beam at B to B' .

If, now, there are any loads W, W_1 , etc. on the beam

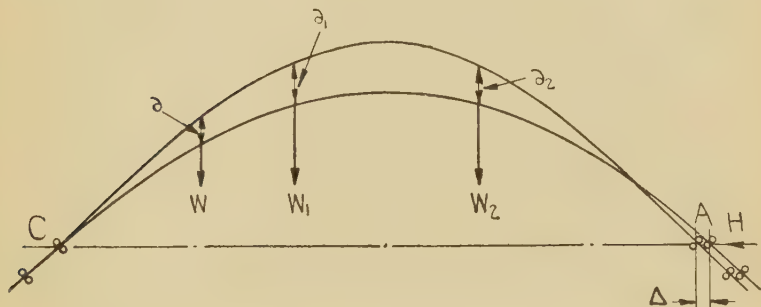
$$R_B\Delta = W\partial + W_1\partial_1 + W_2\partial_2 + \dots,$$

the sign of ∂ being positive when measured downwards and negative when measured upwards. Or, the curve A, B', C, D, E is the influence line for the reaction

at B. If the reactions of a rigid arch are required a model can first be displaced horizontally at A (fig. 4). Then

$$H\Delta = W\partial + W_1\partial_1 + W_2\partial_2,$$

Fig. 4.



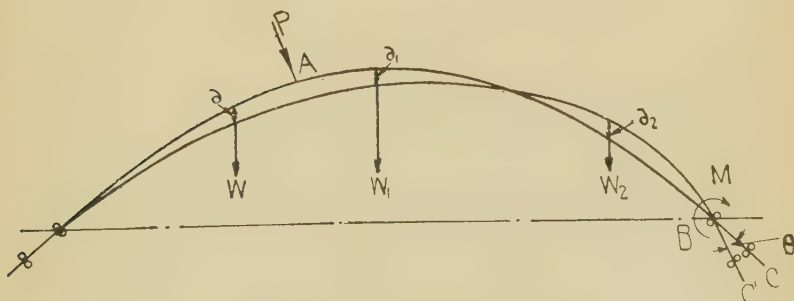
the correct sign being given to ∂ , ∂_1 , etc.; in this case they are all positive.

To determine the reaction moment at B (fig. 5) the tangent BC at B is turned through an angle θ .

Then the fixing couple M at B is given by

$$M\theta = W\partial + W_1\partial_1 + W_2\partial_2 + \dots$$

Fig. 5.



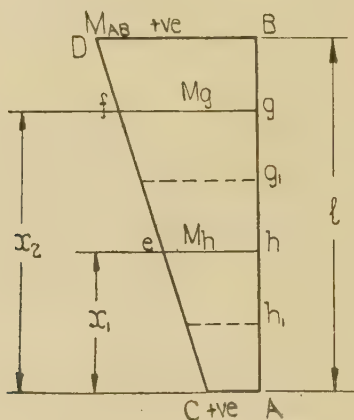
By plotting ∂_1 , ∂_2 , etc. on a horizontal base an influence line for the horizontal reactions at A (fig. 4), or for the fixing moment at B (fig. 5), can be respectively drawn. This method has been developed by Beggs. Very simple

models, in which displacements sufficiently large to be measured without special devices, can be used by students or in the drawing office from which results of sufficient accuracy can be obtained; or more precise models, in which displacements are measured by micrometers or by optical methods, can be made. For certain types of structures the author prefers another method which he has used for some years, and which with care gives excellent results, displacements being measured optically.

The Slope-deflexion Method.

The moments in certain types of indeterminate structures can be determined from the relationship

Fig. 6.



between the relative slopes (see fig. 7) at any points A and B on a structure, and the area of the bending-moment diagram between A and B.

Consider any member AB of a structure (fig. 6), the "second moment" of any section being I. The relative angular movement $\partial\theta$ of any two sections ∂S apart is $\partial\theta = \frac{\partial S}{R}$, where R is the radius of curvature produced by the bending or, $\partial\theta = \frac{M \partial S}{EI}$. The total relative movement of two sections, A and B, is

$$\theta = \int \frac{M \partial S}{EI}.$$

If any section of a straight member is defined by the coordinate x from any origin

$$EI \frac{d^2y}{dx^2} = M, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

then

$$EI \left[\frac{dy}{dx} \right]_{x_1}^{x_2} = \int_{x_1}^{x_2} M dx, \quad . \quad . \quad . \quad . \quad (2)$$

or if θ_1 and θ_2 be the slopes at x_1 and x_2 respectively,

$$EI(\theta_2 - \theta_1) = \text{the area of the bending-moment diagram between } x_1 \text{ and } x_2. \quad . \quad . \quad (3)$$

If AB is not loaded transversely and the moment due to end thrust is neglected, the bending-moment diagram (fig. 6) due to the end fixing couples at A and B will be ACDB.

The area

$$\int_{x_1}^{x_2} M dx = e f g h,$$

$$\theta_2 - \theta_1 = \frac{1}{2}(Mg + Mh)(x_2 - x_1),$$

$$\theta_2^1 - \theta_1^1 = \frac{1}{2}(Mg_1 + Mh_1)(x_2 - x_1),$$

or if M_{BA} and M_{AB} be the respective end couples

$$\theta_2 - \theta_1 = \left\{ \frac{M_{BA}}{l} (x_2 - x_1) + M_{AB} \left(\frac{2l - x_2 - x_1}{l} \right) \right\} \frac{x_2 - x_1}{2}. \quad (4)$$

When $x_2 = l$ and $x_1 = 0$,

$$\frac{1}{2}(M_{BA} + M_{AB})l = \theta_B - \theta_A. \quad . \quad . \quad . \quad . \quad (5)$$

If the element is loaded with a single load W the bending-moment diagram for the element will be as in fig. 6 a, and

$$\begin{aligned} & \theta_{x_2} - \theta_{x_1} \\ &= \left\{ \frac{M_{BA}}{l} (x_2 - x_1) + M_{AB} \left(\frac{2l - x_2 - x_1}{l} \right) \right\} \frac{x_2 - x_1}{2} - h k E m g. \quad (6) \end{aligned}$$

If $x_2 < a$,

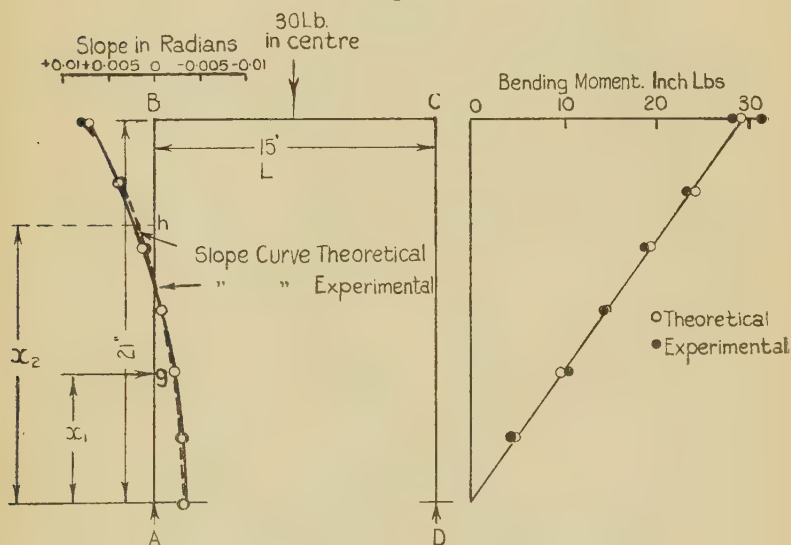
$$h k E m g = \frac{W a b}{l} \frac{x_2^2 - x_1^2}{2a}.$$

relative slopes at any two points g and h the area of the bending-moment diagram, if the diagram is assumed to be linear, can readily be found from equations (4) or (6).

Example.

A three leg-bent (fig. 7) was loaded at the centre of the beam with a load of 30 lb., and the slopes measured optically by the method described later. During the loading the slopes were proportional to the load. The

Fig. 7.



Three unit frame centrally loaded.

relative slopes at two points g and h were obtained, and also at two other points g_1 and h_1 . The value of EI for the material was obtained by direct experiment. The length of AB was 21 inches ; $EI = 29,100$ lb. in.².

By measurement,

$$\left. \begin{array}{l} x_2 = 10.5 \\ x_1 = 3.5 \end{array} \right\} \theta_2 - \theta_1 = 0.00229 \text{ radians,}$$

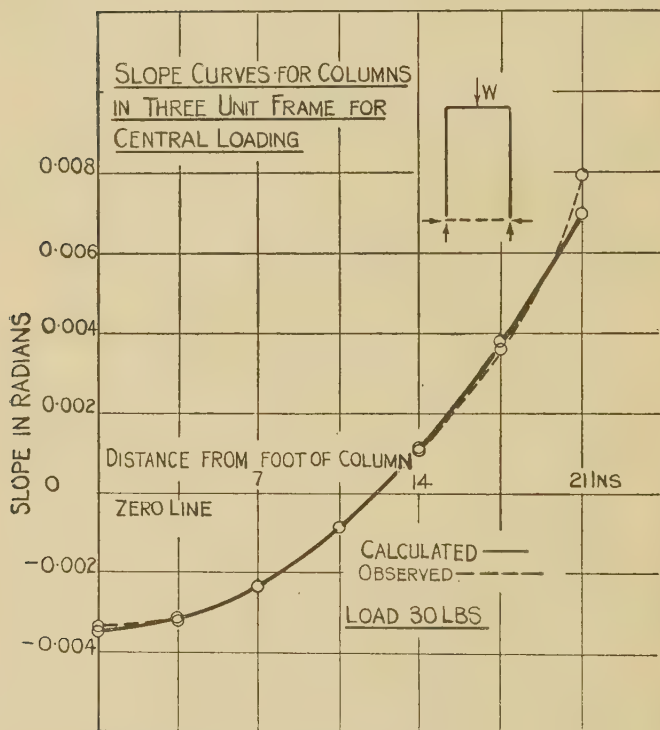
$$\left. \begin{array}{l} x_2 = 17.5 \\ x_1 = 3.5 \end{array} \right\} \theta_2 - \theta_1 = 0.00596 \text{ radians.}$$

890 Prof. F. C. Lea on *Forces and Moments in*
 Substituting in equation (4) the two equations

$$\frac{7}{5}M_{BA} - \frac{14}{3}M_{AB} = 29,100 \times 0.00229,$$

$$\frac{49}{8}M_{BA} - \frac{35}{8}M_{AB} = 29,100 \times 0.00596$$

Fig. 8.



are obtained, from which

$$M_{BA} = 28.18 \text{ in. lb.},$$

$$M_{AB} = -0.1894 \text{ in. lb.}$$

The theoretical value of the bending moment at B is

$$M_{BA} = \frac{3WL}{8(2n+3)},$$

in which

$$n = \frac{l}{L} = \frac{21}{15}, \quad \text{and} \quad M_{AB} = 0.$$

The theoretical value of $M_{AB} = 29.1$ in. lb. as compared with 28.18 in. lb. obtained from the experiment.

Other experimental values can be taken and new values obtained from which a mean value of M_{BA} can be found.

The angular readings can, however, be plotted, as in figs. 7 and 8, and their experimental errors partly eliminated.

TABLE I.

Calculated and Experimental Values of the Bending Moments for the vertical of a three legged frame, assuming the bending moment at the foot zero. $EI = 29,100$ lb. in.².

Distance x_2 from foot of column. Point.	Inches.	Measured slope. Radians.	Bending moment at distance x_2 from foot of column.	
			Calculated.	Experimental.
1	0	0.0034	0	0
2	3.5	0.00314	4.85	4.3
3	7.0	0.00234	9.7	10.4
4	10.5	0.00085	14.5	14.2
5	14.0	0.00106	19.4	18.6
6	17.5	0.00362	24.2	23.3
7	21.0	0.00794	29.1	31.4

If the bending moment at the lower end of the column is assumed zero the bending moments can be calculated. The straight line (see fig. 7 and also Table I.) drawn through the points agrees well with the theoretical values. When the load of 30 lb. was placed eccentrically on the beam the curves showing the slopes obtained by experiment at the nearer column and by calculation were very similar to fig. 8. Taking experimental values at random for the eccentric loading,

$$\left. \begin{array}{l} x_2 = 10.5 \\ x_1 = 3.5 \end{array} \right\} \theta_2 - \theta_1 = 0.00224 \text{ radians,}$$

$$\left. \begin{array}{l} x_2 = 17.5 \\ x_1 = 7.0 \end{array} \right\} \theta_2 - \theta_1 = 0.00580 \text{ radians.}$$

From equation (4)

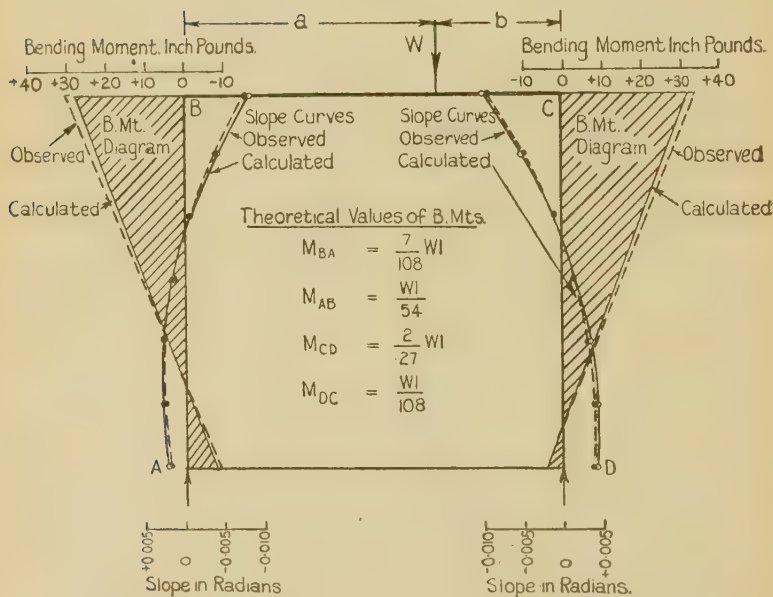
$$\frac{7}{3}(M_{BA} - 2M_{AB}) = 29,100 \times 0.00224,$$

$$\frac{21}{12}(3.5M_{BA} - 2.5M_{AB}) = 29,100 \times 0.0058,$$

$$M_{BA} = 27.344 \text{ in. lb.},$$

$$M_{AB} = -0.2956 \text{ in. lb.}$$

Fig. 9.



The theoretical values are $M_{AB} = 0$, and

$$M_{BA} = \frac{3Wab}{2L(2n+3)},$$

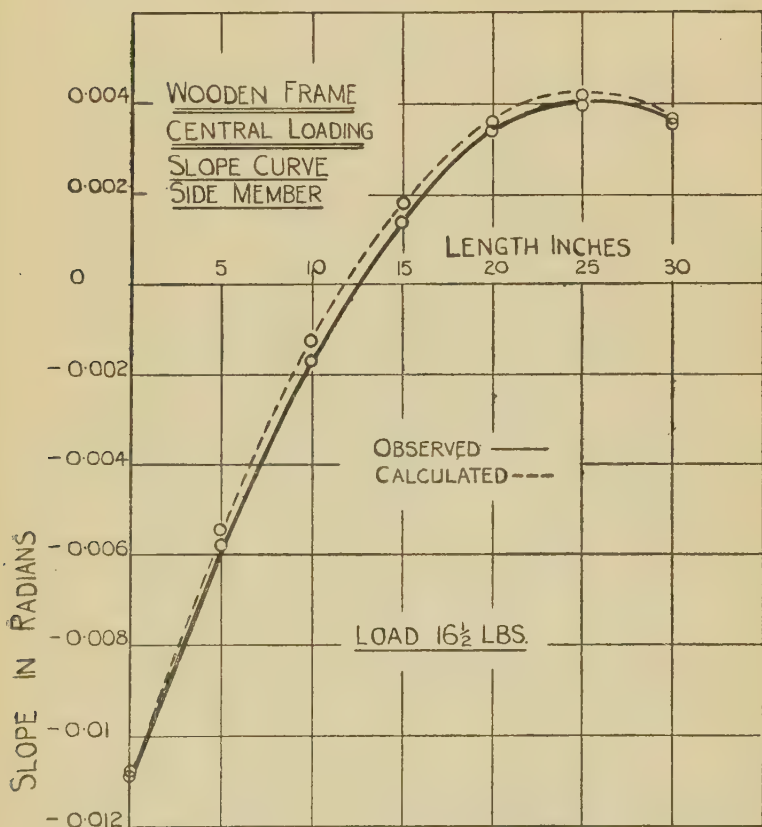
where a and b are the parts into which the load W divides the span. Then

$$M_{AB} = 25.9 \text{ in. lb.}$$

The error is of the order of 5 per cent., but by drawing the curves similar to fig. 8 the experimental errors can be considerably reduced.

The calculated and experimental values are shown plotted in fig. 7. The calculated values at the top and base of the column from equation (4), taking two experimental values for x_2 and x_1 , haphazard from the table, were 28.18 and 0.1894 lb. in. respectively.

Fig. 10.

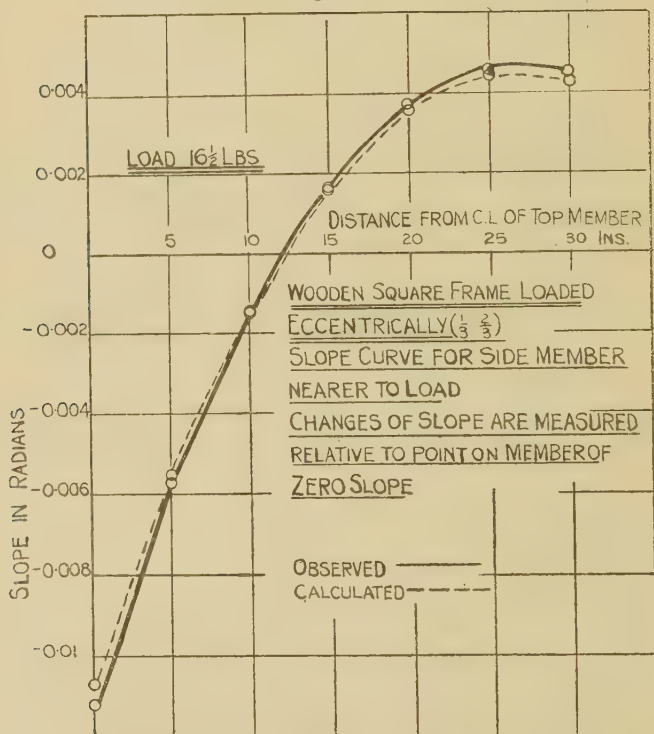


Metal and Wooden Square Frames.

A square frame, 12 inches square, cut from a duralumin plate, $\frac{1}{4}$ -inch thick and $\frac{1}{4}$ -inch wide, was made. The upper beam of the duralumin square was loaded, as in fig. 9. A wooden frame of yellow pine $\frac{3}{4}$ -inch square in section was also made. The slopes as calculated and

observed for the duralumin frame loaded eccentrically are shown plotted in fig. 9. The theoretical bending-moment diagrams and the bending-moment diagrams, assuming these to be straight lines and M_{AB} and M_{BA} calculated from equation (4), are given in fig. 9. The theoretical and experimental slopes for the wooden frame 30 inches square, of yellow pine, are shown in figs. 11 and 12. Models

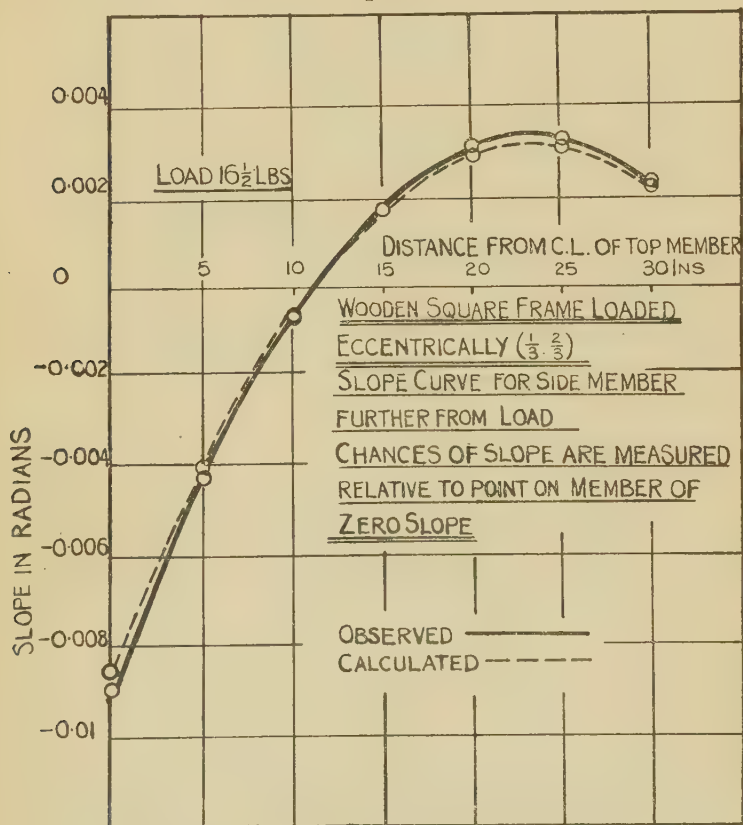
Fig. 11.



of continuous beams supported on columns, and other types of structures have also been examined. The experimental method described fulfils a double purpose. It gives a means of checking the validity of the assumptions made in calculating the moments in statically indeterminate structures, and the results from simple frames give confidence in the experimental analysis of much more complicated structures, the calculations for which are exceedingly laborious, as, for example,

the frame already referred to, fig. 2, or structures with special joints. It is also not difficult to adjust, in the models, the degree of constraint at the ground or at other supports and thus find the effect of various assumptions. It is also possible to check by experiment relative deflexions given by * calculation, using the experimental

Fig. 12.



* From equation (1)

$$EI \frac{d^2 y}{dx^2} x = Mx$$

and

$$EI \int_{x_1}^{x_2} \left[x \frac{dy}{dx} - y \right] = \int_{x_1}^{x_2} Mx dx,$$

$$EI \{ x_2 \theta_2 - y_2 - x_1 \theta_1 + y_1 \} = \int_{x_1}^{x_2} Mx dx.$$

bending moments. For example, three Ames's dials were placed along the side of the square duralumin and wooden

Fig. 13.

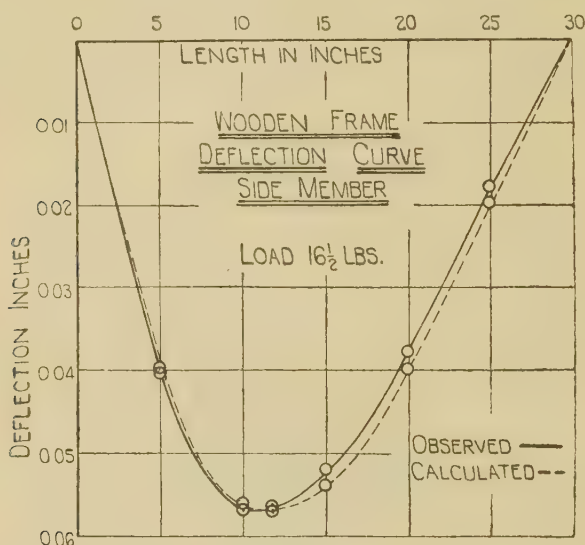
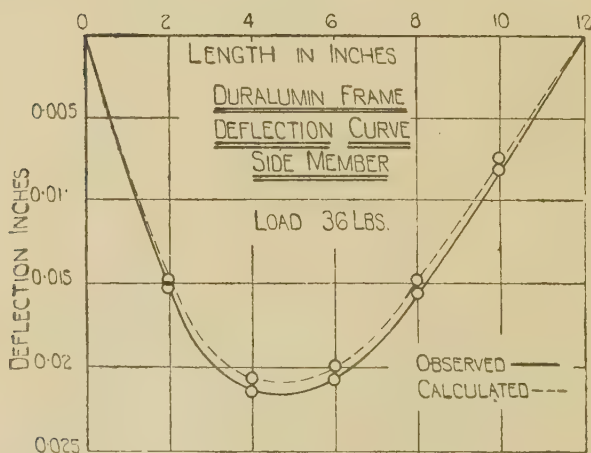


Fig. 14.

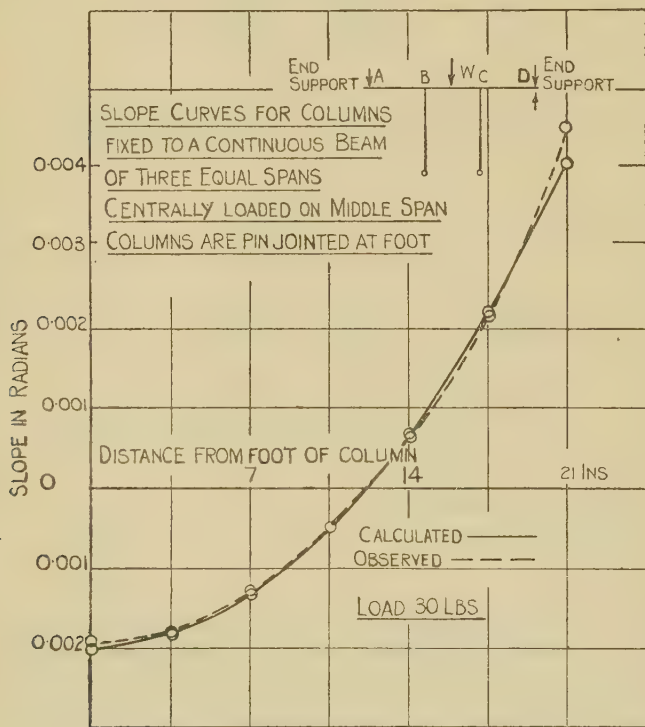


frames respectively. The relative deflexions obtained by calculation are shown compared with experimental values in figs. 13 and 14.

Continuous Beams on Columns.

The theoretical bending-moment diagrams for a load on the central span of a three-span beam resting on two columns and supported at the ends A and D are shown in fig. 20. When the load W was placed at the centre of the middle span the experimental and calculated values of the slopes were as shown in fig. 15. Reference

Fig. 15.



is made later to the comparison between the theoretical and experimental slopes of the columns when the load was placed at the outer span AB, and the importance of friction at A and D is pointed out.

APPARATUS.

*Determination of Modulus of Elasticity
and Values of EI.*

The Modulus of Elasticity, or the values of EI , can be determined experimentally by a number of methods.

Fig. 16 shows a method in which two mirrors, a scale, and telescope are used in the same manner as in the experimental analysis of the structural forms. The bar was of the same dimensions as the elements of the square frame to which reference has already been made.

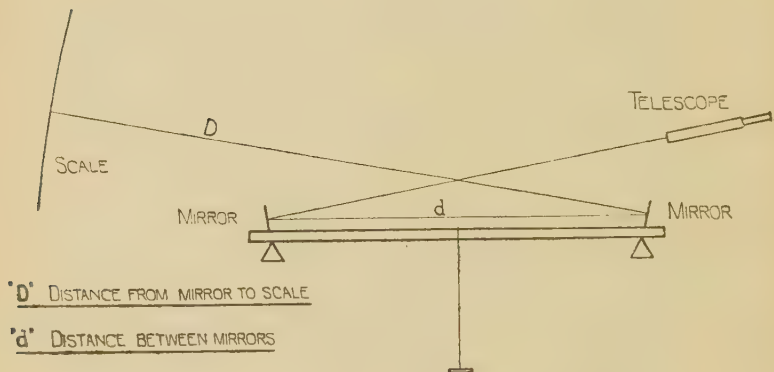
$$\theta_2 - \theta_1 = \frac{\text{scale reading}}{2d + 4D},$$

and

$$EI(\theta_2 - \theta_1) = \frac{Wl^2}{8}.$$

A test of a duralumin beam, 10 inches span, loaded at the centre gave a value of E of 5000 tons per square inch.

Fig. 16.



Two tests of similar beams of 12 inches span, made of bars $\frac{1}{2}'' \times \frac{1}{4}''$, loaded at the centre and deflexions measured under the loads, gave a value of E of 4977 tons per square inch when the beam was loaded so that it was $\frac{1}{2}''$ deep, and 4945 tons per square inch when it was loaded as a beam $\frac{1}{4}''$ deep. The value of EI for the wooden beam $\frac{5}{8}''$ square was 29,100 lb. in.^2 .

Apparatus for Loading Frames—Square Frames.

The frames were supported on rollers in a horizontal plane and could be loaded so that the supports (columns) were either in tension or compression. A stout supporting board was used to support the frames with battens screwed to the back. A planed angle was fixed at one

edge. The square frame when loaded pressed against rollers resting on this angle so that the external moment at the support was very small. The loading to the frame was made through the lever, fig. 18, to which were fixed three knife edges. The lower one rested on a stirrup fixed to the supporting board, the intermediate one rested on the frame under test, and on the uppermost knife-edge a small stirrup rested to which was attached a cord passing over a pulley carried on ball bearings. In place of the intermediate knife-edge it was found convenient

Fig. 17.

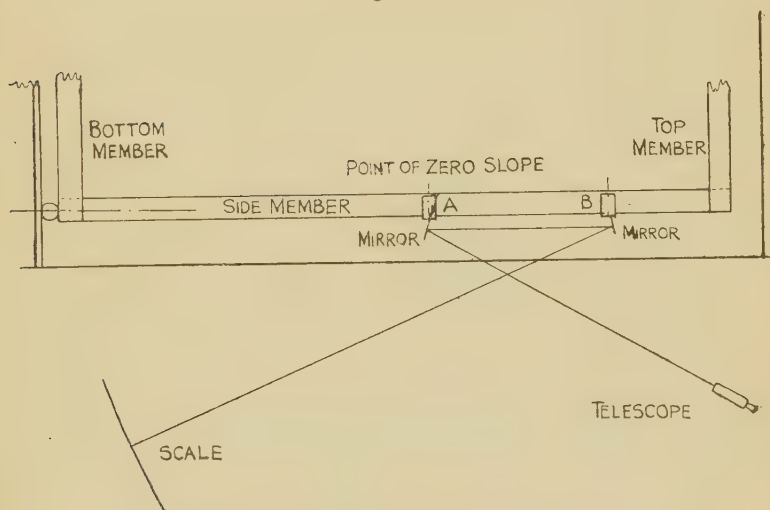


Diagram showing method of measuring change of slope relative to point of zero slope.

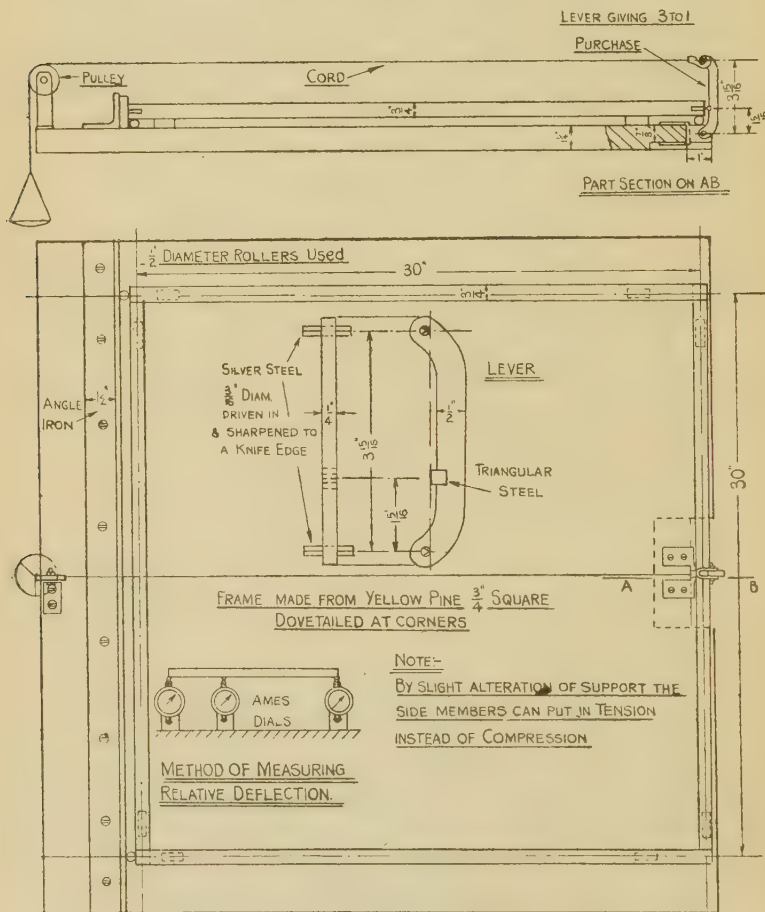
sometimes to use a steel ball. Care must be taken to eliminate friction.

Changes of Slope.

The changes of slope as the load was increased on the model were measured as in fig. 17, one mirror being fixed as near as possible to a point on the element at which the change of slope was zero. Stainless steel mirrors mounted in duralumin frames are found the most suitable. The scale, divided into $1/50$ inch, was set up at approximately 100 inches from the mirror and the telescope

near to the moving mirror. Two telescopes focussed on to the same scale or on to separate scales can be used, the difference in the angular movements being readily obtained. When the mirror is 100 inches from the scale

Fig. 18.



Arrangement for loading frame.

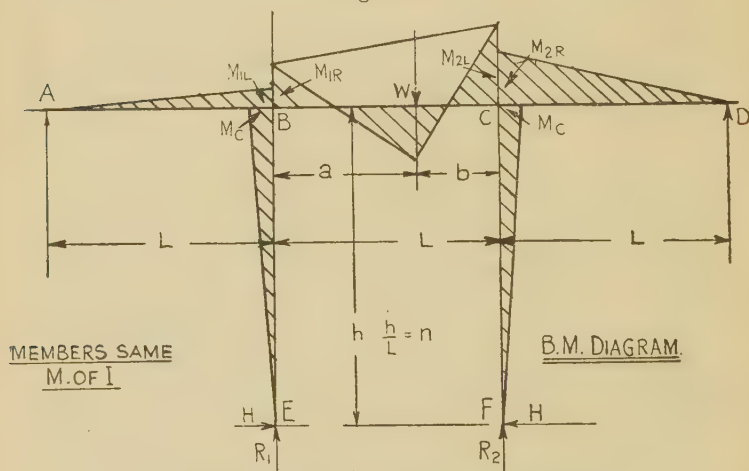
readings can be made to $1/50$ inch with a reasonably good telescope, and angular movements of $1/50 \times 200$ radians can thus be read with the telescope on to one mirror. If EI has a value of $30,000 \text{ lb. in.}^2$, then

and at the other end 30-in. lb., the error in the bending moment due to uncertainty of scale reading will be less than 2 per cent. More precise readings can easily be made if thought desirable, but accuracies of this order are certainly quite sufficient as a basis for structural design.

*The Importance of Friction in certain
Types of Structures.*

In calculations to determine the bending moment on structures due to vertical loads the effect of frictional

Fig. 20.



Continuous beam of three equal spans fixed to two
pin-jointed columns. Load on central span.

forces at the supports is neglected. For example, a girder simply supported; the neutral axis of the girder may be at a height d above the bearing plate and due to friction, therefore, there may be a moment equal to $\mu R d$ acting at the support; μ is the coefficient of friction, and R the reaction at the support. In a structure of the form shown in figs. 19 and 20 the horizontal reactions at the supports A and D may become important as affecting the bending moments on the columns. Suppose, for example, that the beam AB (fig. 20) is loaded. If, then, the supports at A and D are frictionless the bending moments on the two columns are the same. If, however, there is friction

at A or at the point of application of the load then the part ABE may act as a knee and the bending moment on the two columns will be different, *i. e.*, the bending moment on AE is greater than if there is no friction at A or D. The bending moment on CF may be zero or very small. The only satisfactory support at A or D is a practically frictionless roller. On the assumption that A and D were frictionless and with a load of $16\frac{1}{2}$ lb. on AB, at two-thirds of the span from A, the calculated value of the difference of slope ($\theta_B - \theta_E$) at the ends of each of the columns was 0.004382 radians. During one set of experiments the end A did not apparently roll, and there was constraint on the application of the load; the measured value of $\theta_B - \theta_E$ was 0.00763 radian, and of $\theta_C - \theta_F$ was 0.00115 radian. The mean experimental value was 0.00439. The bending moment M_{BE} at the end B of the column was 21 in. lb. and M_{CF} at the point C was only 3.15-in. lb. Assuming the end A to be fixed horizontally and the horizontal reactions at E and A equal the work done by bending on the knee ABE when there is a load W at distance a and b respectively from A and B is

$$U = \int_0^L \frac{Hx^2 dx}{2EI} + \int_0^a \left(\frac{Hlx}{L} - \frac{Wbx}{l} \right)^2 \frac{dx}{EI} \\ + \int_0^b \left(\frac{He}{L}(L-x) - \frac{Wax}{L} \right)^2 \frac{dx}{2EI};$$

$$\frac{dU}{dH} = 0, \text{ when}$$

$$a = \frac{2}{3}L, \quad b = \frac{1}{3}L, \quad \frac{h}{L} = \frac{7}{5}, \quad H = \frac{152}{2268}W.$$

When

$$a = \frac{1}{3}L, \quad b = \frac{2}{3}L, \quad H = \frac{100}{2268}W.$$

The vertical reaction at A is

$$\frac{Wb}{L} - \frac{Hh}{L}.$$

If, then,

$$\mu \left(\frac{Wb}{L} - \frac{Hh}{L} \right) > H,$$

the frame ABC will practically behave as a knee.

In the model to which reference has been made (fig. 19), the bending moment M_{BE} when ABE acts as a knee is about 20 in. lb., which agreed moderately well with the bending moment obtained experimentally.

When the load W is at $\frac{2}{3}L$ from A and $h = \frac{5}{5}L$ the limiting value of μ for ABE to act as a knee is

$$\mu = \frac{\frac{125}{2268} L}{\left(\frac{b}{L} - \frac{125}{2268} \frac{h}{L} \right)},$$

or $\mu = 0.214$.

If there are loads W at $\frac{1}{3}$ and $\frac{2}{3}$ points of the span L respectively the limiting value of $\mu = 0.087$.

It would appear desirable, therefore, when such frames are being designed and there is a possibility of the span being loaded, to calculate the bending moment in the column BE on the assumption that ABE acts as a knee, or if a model is to be used to investigate the bending moments the frictional conditions at A and D should compare with those of practice. Again, it is possible in the model to give varying degrees of fixity to the girder at A and D , and to the columns at E and F .

When structures such as the frame shown in fig. 2 are to be investigated it is quite possible to insure that there is no angular movement of the columns relative to the fixed support, near these supports, or by placing mirrors on the columns and on the supports the relative angular displacement can be found. The experimental method allows, therefore, the fundamental assumptions in some cases to be verified and thus gives confidence in determining the bending moments in structures, the calculations for which are long and laborious, and in which at joints and supports the theoretical conditions may not be approximately fulfilled. The method could also be used to determine the bending moments produced in elements of structures as they are loaded, and it may be adapted to determine, particularly in unloaded elements, the bending moments due to travelling loads.

LXXIII. *The Magneto-Optical Dispersion of Organic Liquids in the Ultra-violet Region of the Spectrum.*—Part V. *The Magneto-Optical Dispersion of Normal Propyl Propionate, Isobutyl Acetate, Ethyl Acetoacetate, and Ethyl Oxalate.* By A. DE M. BEANLAND, M.Sc., and Prof. E. J. EVANS, D.Sc., *Physics Department, University College of Swansea* *.

THE apparatus and experimental methods employed in these investigations have been described in detail in Part I.†, and consequently only a brief reference to these points is necessary.

The light from a tungsten arc falls on a Bellingham-Stanley polarizing unit designed for work in the ultra-violet, and then traverses the liquid contained in a quartz polarimeter tube, which is placed symmetrically inside the core of a solenoid. The polarized beam, after emerging from the liquid, passes through the analyser and a quartz fluorite lens, which brings it to a focus on the slit of a quartz spectrograph. As the beam of light emerging from the polarizer consists of two semicircular fields with a horizontal line of demarcation, the vibrations in one of the fields being polarized at a slight angle with those in the other, two spectra (one immediately above the other) are obtained at the camera end of the quartz spectrograph.

The analyser is set at zero by adjusting its position so that these two spectra have the same intensity throughout their length when the magnetic field of the solenoid is not excited. There are four positions of the analyser for which this is possible, but one of the two positions of minimum intensity is chosen, as the polarimeter is then in its most sensitive position. The analyser is then rotated through an angle θ , and a photograph taken with the magnetic field excited. A second photograph was also taken on the same plate, corresponding to a rotation θ on the opposite side of the zero with the magnetic field reversed. An examination of the photographic plate shows that there is a line of definite wave-length, which has the same intensity in the upper and lower half of each

* Communicated by the Authors.

† Stephens and Evans, *Phil. Mag.* x. p. 759 (1930).

spectrum. Let λ be the mean wave-length of this line, as determined from the photograph, and θ_1 the rotation at this wave-length due to the quartz ends of the polarimeter tube : then the value of Verdet's constant δ of the liquid for wave-length λ is given by the equation

$$\theta_2 = \theta - \theta_1 = \delta \Sigma Hl,$$

where the summation is taken over the length of the liquid column. The current passing through the solenoid was kept constant at two amperes, and the magnetic field H at different points along the axis of the solenoid had been accurately measured. The value of ΣHl was 13398 ± 22 cm. gauss.

The refractive indices of the four liquids in the visible region of the spectrum were determined by means of an accurate spectrometer in the usual manner, and in the ultra-violet region of the spectrum photographically by means of the quartz spectrograph in which the Cornu prism had been replaced by a hollow glass prism closed by plates of optically worked fused quartz.

The results obtained by the two methods overlapped over a region of the visible spectrum. The mode of procedure in the photographic determinations was as follows :—

Three slightly overlapping copper spectra were photographed with the hollow prism filled with (a) the standard liquid, (b) the liquid under investigation, and (c) the standard liquid. The standard liquids employed were normal butyl alcohol and iso-amyl alcohol, whose refractive indices in the visible and ultra-violet regions of the spectrum had been determined by Stephens and Evans *, and Thomas and Evans † respectively. The refractive index of the liquid under investigation for a wave-length λ_2 can be determined by identifying, in the spectrum produced by the standard liquid, a line of wave-length λ_1 , which coincides in position with the line of wave-length λ_2 in the spectrum of the liquid under investigation. Then the refractive index of the liquid for a wave-length λ_2 equals the refractive index of the standard liquid for the wave-length λ_1 . The temperatures of the liquids were determined immediately after each

* *Loc. cit.*

† Phil. Mag. xi. p. 1220 (May 1931).

exposure by means of a small calibrated mercury thermometer, and the slight shifts in the positions of the spectra were due to small temperature changes. The values of the temperature coefficients of refractive index of each liquid were found by taking photographs of two slightly overlapping copper spectra by means of the hollow prism containing the particular liquid at two known temperatures. From the resulting displacements in the positions of the spectrum lines, the temperature coefficients corresponding to different regions of the spectrum could be determined. From a knowledge of the temperature coefficients, the refractive indices of the liquids at temperatures differing by a few degrees from those at which they were determined could be calculated.

The liquids employed in this investigation were obtained from Dr. Schuchardt, of Görlitz, and each (with the exception of ethyl acetoacetate, which partially decomposes when distilled at ordinary pressures) was subjected to a process of fractional distillation before determinations were made of the refractive indices and the magneto-optical rotations.

The experimental results have been examined in relation to Larmor's * theory of magneto-optical rotation. According to this theory Verdet's constant δ is given by the expression

$$\delta = \frac{e}{2mC^2} \cdot \lambda \cdot \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the refractive index, $\frac{e}{m}$ is the ratio of the charge to the mass of the resonators, and C the velocity of light. In the above expression the charge e is measured in electrostatic units and the magnetic field in electromagnetic units.

If the magneto-optical dispersion of each of the liquids in the region of the spectrum investigated is controlled by one absorption band in the ultra-violet, and the ordinary dispersion by an equation of the Ketteler-Helmholtz type, it can be shown that

$$\phi = n\delta\lambda^2 = K \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Larmor, 'Æther and Matter,' Appendix F.

where K is a constant and λ_1 the wave-length of the absorption band in the ultra-violet.

In addition, it can be shown by combining equations (1) and (2) and the natural dispersion equation

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2}, \quad \dots \quad (3)$$

that the value of $\frac{e}{m}$ is given by $-\frac{2KC^2}{b_1}$.

EXPERIMENTAL RESULTS.

Ordinary Dispersion.

TABLE I. (a).

Visual Determinations.

Wave-length in microns.	Refractive indices.			
	Propyl propionate at 16.6° C.	Isobutyl acetate at 11.4° C.	Ethyl aceto- acetate at 10.4° C.	Ethyl oxalate at 9.5° C.
.6678	1.3927 ₃	1.3915 ₈	1.4209 ₅	1.4126 ₀
.5876	1.3950 ₂	1.3941 ₅	1.4237 ₆	1.4152 ₇
.5016	1.3988 ₉	1.3977 ₁	1.4282 ₅	1.4194 ₆
.4922	1.3992 ₉	1.3984 ₈	1.4288 ₇	1.4201 ₃
.4713	1.4006 ₉	1.3996 ₂	1.4304 ₄	1.4216 ₀
.4472	1.4024 ₇	1.4013 ₂	1.4327 ₉	1.4235 ₆

Magneto-Optical Dispersion.

Normal Propyl Propionate.

The specimen of propyl propionate employed for the magneto-optical experiments distilled over between 123.2° C. and 123.4° C. at a pressure of 761.5 mm. of mercury, its normal boiling-point being 123.4° C.*. The experimental results are given in Table II. (a) and fig. 3.

* 'International Critical Tables,' i. p. 203.

TABLE I. (b).
Photographic Determinations.

Propyl propionate at 16.6° C.		Isobutyl acetate at 11.4° C.		Ethyl acetoacetate at 10.4° C.		Ethyl oxalate at 9.5° C.	
Wave-length.	Refractive index.	Wave-length.	Refractive index.	Wave-length.	Refractive index.	Wave-length.	Refractive index.
·4587	1.4015 ₈	·4275	1.4033	·5782	1.4242 ₇	·5782	1.4156 ₈
·4275	1.4042 ₁	·4247	1.4036	·5106	1.4275 ₈	·5153	1.4186 ₈
·4023	1.4068 ₁	·4043	1.4057	·4866	1.4293 ₂	·4866	1.4204 ₃
·3821	1.4093 ₆	·4018	1.4060 ₃	·4705	1.4304 ₉	·4705	1.4216 ₈
·3688	1.4114 ₁	·3846	1.4081 ₆	·4480	1.4327 ₂	·4587	1.4225 ₁
·3601	1.4127 ₆	·3825	1.4084 ₈	·4378	1.4338 ₄	·4378	1.4243 ₆
·3510	1.4141 ₆	·3689	1.4104 ₈	·4275	1.4349 ₇	·4275	1.4255 ₃
·3338	1.4175 ₉	·3584	1.4122 ₄	·4201	1.4358 ₇	·4178	1.4266 ₃
·3247	1.4197 ₁	·3566	1.4125 ₆	·4100	1.4370 ₇	·4067	1.4279 ₃
·3208	1.4207 ₁	·3532	1.4131 ₆	·4004	1.4385 ₇	·3861	1.4307 ₃
·3044	1.4253 ₀	·3462	1.4144	·3861	1.4408 ₇	·3688	1.4334 ₃
·2961	1.4280 ₆	·3337	1.4168 ₅	·3735	1.4432 ₇	·3600	1.4352 ₃
·2883	1.4308 ₆	·3247	1.4189			·3532	1.4364 ₃
·2824	1.4330 ₆	·3194	1.4202			·3468	1.4377 ₆
·2766	1.4353 ₈	·3126	1.4222			·3413	1.4389 ₃
		·3073	1.4235 ₃			·3351	1.4404 ₃
		·2997	1.4260 ₃			·3267	1.4427 ₃
		·2961	1.4272 ₇				
		·2859	1.4308 ₉				
		·2824	1.4322 ₈				
		·2766	1.4348				

TABLE I. (c).*

Liquid.	Temp. coefficient of refractive index.
Propyl propionate	·0004 ₃ per ° C.
Isobutyl acetate	·0004 ₃ „
Ethyl acetoacetate	·0004 ₄ „
Ethyl oxalate	·0004 ₆ „

* The refractive indices given in Tables I. (a) and I. (b) were determined at about 20° C., and were corrected by means of the results given in I. (c).

Fig. 1.

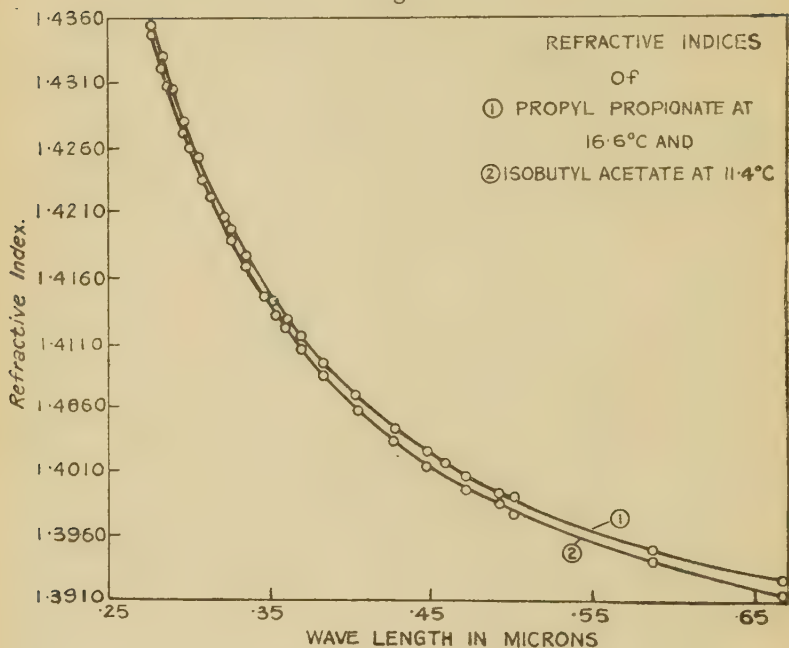


Fig. 2.

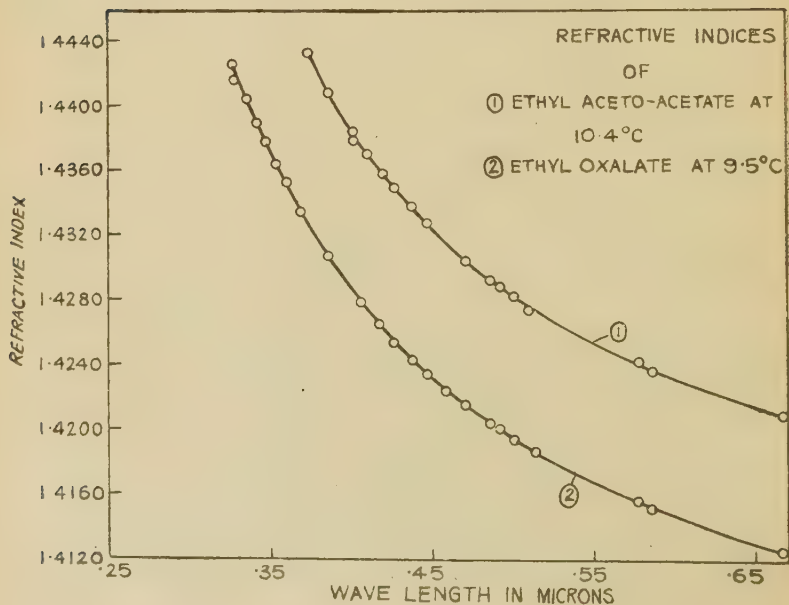


TABLE II. (a).

Values of Verdet's constant for Propyl Propionate
at various wave-lengths.

Temperature = 16.6° C.

Wave-length in microns.	Verdet's constant in mins./cm. gauss.	Wave-length in microns.	Verdet's constant in mins./cm. gauss.
·4586	·0198 ₇	·3660	·0331 ₄
·4530	·0204 ₂	·3609	·0342 ₅
·4472	·0209 ₇	·3562	·0353 ₄
·4423	·0215 ₂	·3518	·0364 ₆
·4372	·0220 ₇	·3472	·0375 ₅
·4278	·0231 ₈	·3431	·0386 ₇
·4190	·0242 ₉	·3390	·0397 ₇
·4110	·0253 ₉	·3352	·0408 ₉
·4033	·0265 ₀	·3315	·0419 ₈
·3961	·0276 ₁	·3281	·0431 ₀
·3890	·0287 ₁	·3246	·0442 ₀
·3832	·0298 ₂	·3215	·0453 ₂
·3772	·0309 ₂	·3181	·0464 ₁
·3713	·0320 ₄		

TABLE II. (b).

λ in microns.	δ mins./cm. gauss.	n .
(a)	·4372	·0220 ₇
(b)	·3660	·0331 ₄
(c)	·3246	·0442 ₀

Table II. (b) gives a series of values of n , the refractive index, and δ , Verdet's constant, taken from fig. 1 and Table II. (a) respectively. It was found that the experi-

mental results could be represented by a formula of the type

$$\phi = n\delta\lambda^2 = K \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2,$$

and from several pairs of values of ϕ and λ the values of λ_1 and K were obtained.

The values of the function ϕ were calculated for each wave-length, and the following pairs used to obtain the constants :—

From (a) and (b), $\lambda_1 = .1087 \mu$ and $K = 5.211 \times 10^{-3}$.
 „ (b) „ (c), $\lambda_1 = .1089 \mu$ „ $K = 5.207 \times 10^{-3}$.
 „ (a) „ (c), $\lambda_1 = .1088 \mu$ „ $K = 5.209_4 \times 10^{-3}$.

The mean values of λ_1 and K are $.1088 \mu$ and 5.209×10^{-3} respectively, δ being measured in minutes per cm. gauss, and λ in microns.

TABLE II. (c).

λ (microns).	δ (observed).	δ (calculated).
.4586	.0198 ₇	.0198 ₄
.4472	.0209 ₇	.0209 ₈
.4278	.0231 ₈	.0231 ₇
.4110	.0253 ₉	.0253 ₆
.3890	.0287 ₁	.0287 ₇
.3772	.0309 ₂	.0309 ₆
.3562	.0353 ₄	.0353 ₃
.3431	.0386 ₇	.0386 ₄
.3315	.0419 ₈	.0420 ₆
.3181	.0464 ₁	.0464 ₅

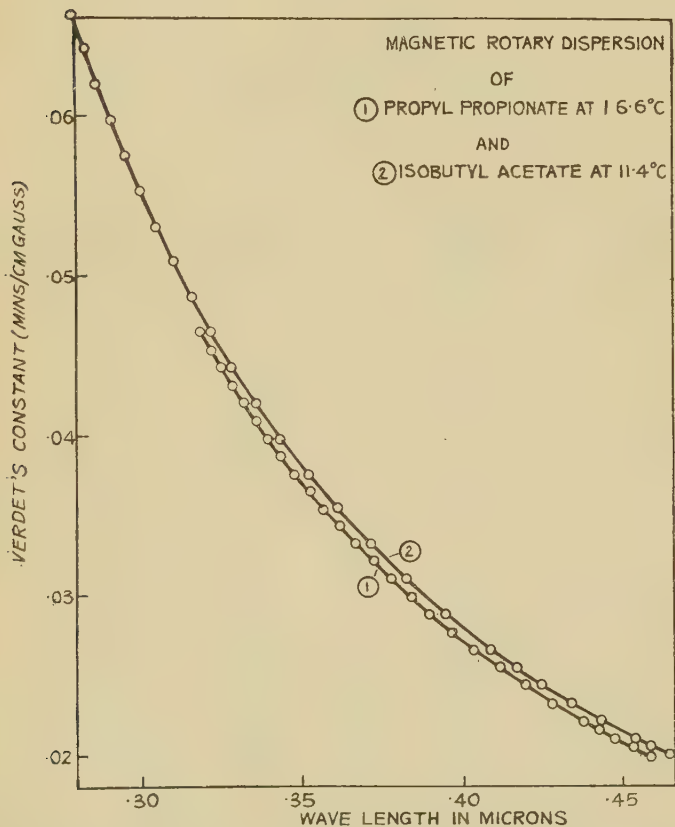
Thus the equation representing the magneto-optical dispersion of propyl propionate at 16.6°C . for the range of the spectrum investigated ($.4586 \mu$ to $.3181 \mu$) is :—

$$n\delta = 5.20_9 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (.1088)^2\}^2}.$$

This equation was used to calculate the value of δ for other wave-lengths where experimental determinations had been carried out. The values of n were read off from fig. 1.

Perkin* found the specific rotation of propyl propionate to be $\cdot 8807$ at 18°C . and $\cdot 8777$ at $21\cdot 5^{\circ}\text{C}$. Taking the value of the temperature coefficient deduced from these results, and the value of Verdet's constant of water for sodium light to be $\cdot 0131$, the value of Verdet's constant

Fig. 3.



of propyl propionate deduced from Perkin's observations is $\cdot 01155$ at $16\cdot 6^{\circ}\text{C}$.

The value for sodium light calculated from the above equation is $\cdot 01153$, which is in good agreement with the observed value.

* Journ. Chem. Soc. xlv. p. 498 (1884).

Isobutyl Acetate.

The isobutyl acetate employed in the determinations of Verdet's constant distilled over between 116.3°C . and 116.8°C . at a pressure of 759.5 mm. of mercury, its normal boiling-point being 116.3°C .† The experimental results are given in Table III. (a) and plotted in fig. 3.

TABLE III. (a).

Values of Verdet's constant for Isobutyl Acetate
at various wave-lengths.

Temperature = 11.4°C .

Wave-length in microns.	Verdet's constant in mins./cm. gauss.	Wave-length in microns.	Verdet's constant in mins./cm. gauss.
·4641	·0198 ₇	·3429	·0397 ₉
·4585	·0204 ₆	·3354	·0420 ₁
·4534	·0209 ₈	·3280	·0442 ₂
·4429	·0220 ₃	·3217	·0464 ₄
·4334	·0231 ₉	·3157	·0486 ₆
·4243	·0243 ₀	·3101	·0508 ₈
·4164	·0254 ₀	·3048	·0530 ₉
·4085	·0265 ₁	·2998	·0553 ₀
·3941	·0287 ₂	·2953	·0575 ₂
·3817	·0309 ₄	·2910	·0597 ₄
·3704	·0331 ₅	·2867	·0619 ₆
·3605	·0353 ₇	·2831	·0641 ₈
·3512	·0375 ₈	·2793	·0664 ₀

In Table III. (b) values of Verdet's constant and the refractive indices corresponding to certain wave-lengths are given. These were employed to calculate the constants of the magneto-optical dispersion equation for isobutyl acetate.

* Beilstein's 'Handbuch der organischen Chemie,' ii. p. 131.

TABLE III. (b).

	λ in microns.	δ in mins./cm. gauss.	n .
(a)	·4243	·0243 ₀	1·4037
(b)	·3429	·0397 ₉	1·4151
(c)	·2793	·0664 ₀	1·4336

From (a) and (b), $\lambda_1 = \cdot 1081_6 \mu$ and $K = 5\cdot 36_9 \times 10^{-3}$.

„ (b) „ (c), $\lambda_1 = \cdot 1079 \mu$ „ $K = 5\cdot 37_4 \times 10^{-3}$.

„ (a) „ (c), $\lambda_1 = \cdot 1080_1 \mu$ „ $K = 5\cdot 37_1 \times 10^{-3}$.

The mean values of λ_1 and K are $\cdot 1080 \mu$ and $5\cdot 37_1 \times 10^{-3}$ respectively, and the equation representing the magneto-optical dispersion of isobutyl acetate over the range of the spectrum investigated ($\cdot 4641 \mu$ to $\cdot 2793 \mu$) is

$$n\delta = 5\cdot 37_1 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (\cdot 1080)^2\}^2}.$$

TABLE III. (c).

λ in microns.	δ (observed).	δ (calculated).
·4641	·0198 ₇	·0199 ₀
·4534	·0209 ₈	·0209 ₆
·4334	·0231 ₉	·0231 ₇
·4085	·0265 ₁	·0264 ₈
·3817	·0309 ₄	·0309 ₃
·3605	·0353 ₇	·0353 ₃
·3354	·0420 ₁	·0419 ₆
·3217	·0464 ₄	·0464 ₄
·3048	·0530 ₉	·0530 ₈
·2953	·0575 ₂	·0575 ₀
·2867	·0619 ₆	·0620 ₃

This equation was used to calculate δ for a few wavelengths at which experimental determinations had been carried out. The values of n used were read off from fig. 1. Table III. (c) shows a comparison of the observed and calculated values.

The value of Verdet's constant for sodium light was calculated from the above equation, and the value obtained was $\cdot 0118_8$.

The specific rotations for sodium light of isobutyl acetate at $9\cdot 4^\circ \text{C}$. and $10\cdot 5^\circ \text{C}$. as determined by Perkin * are $\cdot 9052$ and $\cdot 9074$ respectively. From the temperature coefficient calculated from the above results, and the known value of Verdet's constant of water for sodium

TABLE IV. (a).

Values of Verdet's constant for Ethyl Acetoacetate at various wave-lengths.

Temperature = $10\cdot 4^\circ \text{C}$.

Wave-length in microns.	Verdet's constant in mins./cm. gauss.	Wave-length in microns.	Verdet's constant in mins./cm. gauss.
$\cdot 4719$	$\cdot 0198_8$	$\cdot 4145$	$\cdot 0265_2$
$\cdot 4661$	$\cdot 0204_7$	$\cdot 4072$	$\cdot 0276_3$
$\cdot 4607$	$\cdot 0209_9$	$\cdot 4003$	$\cdot 0287_3$
$\cdot 4547$	$\cdot 0215_7$	$\cdot 3936$	$\cdot 0298_4$
$\cdot 4499$	$\cdot 0220_9$	$\cdot 3874$	$\cdot 0309_4$
$\cdot 4401$	$\cdot 0231_9$	$\cdot 3815$	$\cdot 0320_6$
$\cdot 4309$	$\cdot 0243_1$	$\cdot 3758$	$\cdot 0331_6$
$\cdot 4226$	$\cdot 0254_1$		

light, it can be calculated that Perkin's value of the Verdet's constant of isobutyl acetate at $11\cdot 4^\circ \text{C}$. for sodium light is $\cdot 01191$. This is in good agreement with the value $\cdot 01188$ calculated from the equation.

Ethyl Acetoacetate.

Messrs. Hopkins and Williams supplied the pure specimen of ethyl acetoacetate, which had been redistilled *in vacuo*. The experimental results for the magneto-optical rotations are given in Table IV. (a) and fig. 4.

* Journ. Chem. Soc. xlv. p. 495 (1884).

Table IV. (b) contains results read off from fig. 2 and Table IV. (a), and these were made use of in solving the magneto-optical dispersion equation.

Fig. 4.

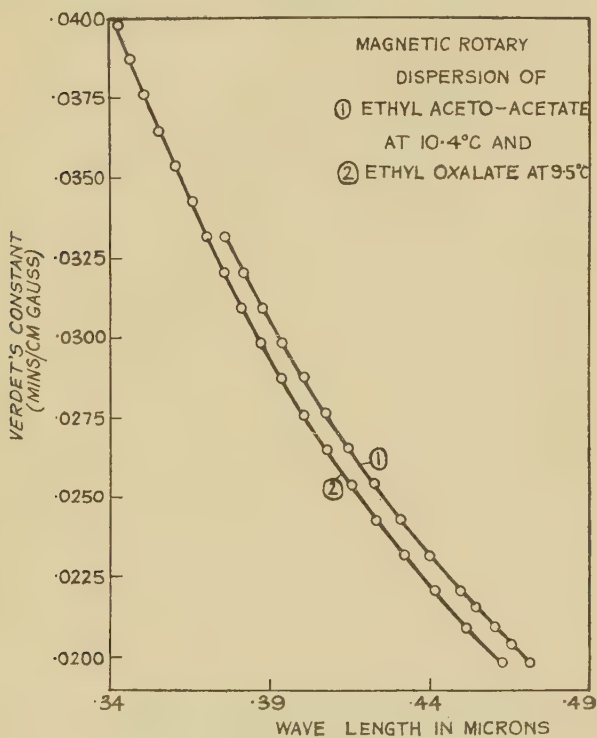


TABLE IV. (b).

	λ in microns.	δ in mins./cm. gauss.	n .
(a)	0.4547	0.0215 ₇	1.4320
(b)	0.4401	0.0231 ₉	1.4335 ₄
(c)	0.3936	0.0298 ₄	1.4396
(d)	0.3815	0.0320 ₅	1.4417

From (a) and (d), $\lambda_1 = .1087_4 \mu$ and $K = 5.675_8 \times 10^{-3}$.

„ (b) „ (c), $\lambda_1 = .1090_6 \mu$ „ $K = 5.671_7 \times 10^{-3}$.

The mean value of $\lambda_1 = .1089 \mu$ and $K = 5.67_4 \times 10^{-3}$, and the equation representing the magneto-optical dispersion of ethyl acetoacetate over the region $.4719 \mu$ to $.3758 \mu$ is

$$n\delta = 5.67_4 \times 10^{-3} \cdot \frac{\lambda^2}{\{\lambda^2 - (.1089^2)\}^2}.$$

The accuracy of the representation of the results by the equation is shown in Table IV. (c), where a comparison

TABLE IV. (c).

λ in microns.	δ (observed).	δ (calculated).
.4719	.0198 ₈	.0198 ₇
.4607	.0209 ₉	.0209 ₅
.4499	.0220 ₉	.0221 ₃
.4309	.0243 ₁	.0243 ₁
.4145	.0265 ₂	.0265 ₂
.4003	.0287 ₈	.0287 ₀
.3874	.0309 ₄	.0309 ₄
.3758	.0331 ₆	.0332 ₀

is made of the experimental values of Verdet's constant and the values calculated from the equation.

The value of Verdet's constant for sodium light was also calculated from the above equation, and was found to be $\delta = .0123_0$. Perkin * determined the specific rotations of ethyl acetoacetate for sodium light at 13.5°C . and 19.5°C ., and obtained the values $.9330$ and $.9227$ respectively. From the temperature coefficient of specific rotation calculated from the above results and the known value ($.0131$) of Verdet's constant of water for sodium light, it can be calculated that Perkin's value of the Verdet's constant of ethyl acetoacetate for sodium

* Journ. Chem. Soc. xlv. p. 493 (1884).

light at 10.4°C . is $\cdot 01229$. This value is in very good agreement with that deduced above.

Ethyl Oxalate.

The ethyl oxalate employed for the determination of the magneto-optical rotations was allowed to stand

TABLE V. (a).

Values of Verdet's constant for Ethyl Oxalate
at various wave-lengths.

Temperature = 9.5°C .

Wave-length in microns.	Verdet's constant in mins./cm. gauss.	Wave-length in microns.	Verdet's constant in mins./cm. gauss.
$\cdot 4631$	$\cdot 0198_7$	$\cdot 3810$	$\cdot 0309_4$
$\cdot 4518$	$\cdot 0209_8$	$\cdot 3756$	$\cdot 0320_4$
$\cdot 4416$	$\cdot 0220_8$	$\cdot 3700$	$\cdot 0331_5$
$\cdot 4320$	$\cdot 0231_9$	$\cdot 3653$	$\cdot 0342_6$
$\cdot 4232$	$\cdot 0242_9$	$\cdot 3600$	$\cdot 0353_7$
$\cdot 4152$	$\cdot 0254_0$	$\cdot 3553$	$\cdot 0364_7$
$\cdot 4077$	$\cdot 0265_1$	$\cdot 3509$	$\cdot 0375_8$
$\cdot 4000$	$\cdot 0276_1$	$\cdot 3465$	$\cdot 0387_2$
$\cdot 3933$	$\cdot 0287_2$	$\cdot 3425$	$\cdot 0397_9$
$\cdot 3871$	$\cdot 0298_3$		

over calcium chloride for some time to remove any possible traces of water. It was then distilled, the main fraction coming over between 185.5°C . and 185.7°C ., when the pressure was 746.2 mm. of mercury, the correct normal boiling-point being 186.1°C .* The experimental results are given in Table V. (a) and fig. 4.

Table V. (b) contains results read off from fig. 2 and Table V. (a), and these were made use of in solving the dispersion equation.

* 'International Critical Tables,' i. p. 201.

TABLE V. (b).

	λ in microns.	δ mins./cm. gauss.	n .
(a)	·4631	·0198 ₇	1·4220 ₄
(b)	·3871	·0298 ₃	1·4305 ₈
(c)	·3425	·0397 ₉	1·4386 ₄

From (a) and (b), $\lambda_1 = \cdot 1114 \mu$ and $K = 5\cdot 376 \times 10^{-3}$.

„ (b) „ (c), $\lambda_1 = \cdot 1095 \mu$ „ $K = 5\cdot 411 \times 10^{-3}$.

„ (a) „ (c), $\lambda_1 = \cdot 1105 \mu$ „ $K = 5\cdot 390 \times 10^{-3}$.

The mean values of λ_1 and K are $\cdot 1105 \mu$ and $5\cdot 392 \times 10^{-3}$ respectively, and the equation representing the magneto-optical dispersion of ethyl oxalate at $9\cdot 5^\circ \text{C}$. over the region of the spectrum investigated ($\cdot 4631 \mu$ to $\cdot 3425 \mu$) is

$$n\delta = 5\cdot 39_2 \times 10^{-3} \cdot \frac{\lambda^2}{\{\lambda^2 - (\cdot 1105)^2\}^2}.$$

TABLE V. (c).

λ in microns.	δ (observed).	δ (calculated).
·4416	·0220 ₈	·0221 ₀
·4232	·0242 ₉	·0243 ₁
·4077	·0265 ₁	·0264 ₇
·3933	·0287 ₂	·0287 ₄
·3810	·0309 ₄	·0309 ₅
·3700	·0331 ₅	·0331 ₃
·3600	·0353 ₇	·0353 ₄
·3509	·0375 ₉	·0375 ₈
·3425	·0397 ₉	·0398 ₁

The accuracy of the representation of the results by this formula is shown in Table V. (c), where the values of Verdet's constant calculated from the formula are compared with the values obtained experimentally.

The value of Verdet's constant for sodium light at 9.5°C ., as calculated from the above equation, is $\cdot 01179$.

According to Perkin * the specific rotation of ethyl oxalate at 12.8°C . for sodium light is 0.8921 , and at 15°C . 0.8880 . If the value of the temperature coefficient deduced from the above results be taken, the calculated value of the specific rotation at 9.5°C . is $\cdot 8983$. Assuming this value for the specific rotation and taking $\cdot 0131$ as the value of Verdet's constant of water for sodium light, Verdet's constant for ethyl oxalate at the same wave-length is $\cdot 01177$. This is in good agreement with the result calculated from the formula.

The Ordinary Dispersion Equations.

The experimental results have shown that the magneto-optical dispersion of each liquid over the range of the spectrum investigated can be explained by the presence of a single absorption band. A satisfactory dispersion equation can be obtained for each of these liquids if the assumption is now made that the same absorption band is responsible for the ordinary dispersion of the liquid over the same range of wave-length.

The constants of the equation of the form

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

can be obtained from two values of the refractive index corresponding to two wave-lengths.

Propyl Propionate.

The mean values of b_1 and b_0 are $\cdot 909_9 \times 10^{-2}$ and $\cdot 9186_7$, respectively, and the natural dispersion equation of propyl propionate at 16.6°C . is

$$n^2 = 1.9187 + \frac{\cdot 910 \times 10^{-2}}{\lambda^2 - (\cdot 1088)^2}.$$

* Journ. Chem. Soc. xlv. p. 508 (1884).

The pairs of values used are given below :—

TABLE VI. (a).

λ in microns.	n .	b_1 .	b_0 .
·6678	1·3927 ₃		
·4275	1·4042 ₁	$\cdot 905_2 \times 10^{-2}$	·9188 ₅
·5876	1·3950 ₂		
·3821	1·4093 ₆	$\cdot 902_8 \times 10^{-2}$	·9190 ₁
·5016	1·3988 ₉		
·3601	1·4127 ₈	$\cdot 903_6 \times 10^{-2}$	·9192 ₁
·4713	1·4006 ₉		
·2961	1·4280 ₆	$\cdot 918_4 \times 10^{-2}$	·9182 ₇
·4472	1·4024 ₇		
·2766	1·4353 ₈	$\cdot 919_7 \times 10^{-2}$	·9180 ₁

This equation was used to calculate n for a number of wave-lengths where experimental values had been obtained. Table VI. (b) contains a comparison of the calculated and experimental values.

TABLE VI. (b).

λ in microns.	n (observed).	n (calculated).
·4922	1·3992 ₉	1·3993 ₄
·4587	1·4015 ₆	1·4016 ₀
·4023	1·4068 ₁	1·4068 ₈
·3688	1·4114 ₁	1·4113 ₆
·3338	1·4175 ₉	1·4177 ₅
·3208	1·4207 ₁	1·4207 ₆
·2961	1·4280 ₆	1·4278 ₁
·2824	1·4330 ₆	1·4327 ₀

Isobutyl Acetate.

The constants b_1 and b_0 of the natural dispersion equation for isobutyl acetate were calculated from the pairs of values given in the following table :—

TABLE VII. (a).

λ in microns.	n .	b_1 .	b_0 .
·6678	1·3915 ₈	$\cdot 924_4 \times 10^{-2}$	$\cdot 9152_2$
·4275	1·4033		
·5876	1·3941 ₅	$\cdot 905_4 \times 10^{-2}$	$\cdot 9165_2$
·3825	1·4084 ₆		
·5016	1·3977 ₁	$\cdot 920_4 \times 10^{-2}$	$\cdot 9152_3$
·3073	1·4235 ₃		
·4713	1·3996 ₂	$\cdot 929_8 \times 10^{-2}$	$\cdot 9147_6$
·2859	1·4308 ₉		
·4472	1·4013 ₂	$\cdot 939_0 \times 10^{-2}$	$\cdot 9138_3$
·2766	1·4348		

The mean value of $b_1 = \cdot 923_8 \times 10^{-2}$ and of $b_0 = \cdot 9151_1$, and the equation representing the natural dispersion of isobutyl acetate at 11·4° C. is

$$n^2 = 1\cdot 9151 + \frac{\cdot 924 \times 10^{-2}}{\lambda^2 - (\cdot 1080)^2}.$$

Values of n calculated from this equation are compared in Table VII. (b) with the observed values at certain wave-lengths.

TABLE VII. (b).

λ in microns.	n (observed).	n (calculated).
·4922	1·3984 ₈	1·3982 ₆
·4247	1·4036	1·4035 ₁
·3846	1·4081 ₆	1·4081 ₅
·3689	1·4104 ₈	1·4104 ₄
·3532	1·4131 ₆	1·4130 ₇
·3337	1·4168 ₅	1·4169 ₅
·3194	1·4202	1·4203 ₃
·2997	1·4260 ₃	1·4259 ₂
·2824	1·4322 ₈	1·4320 ₅

Ethyl Acetoacetate.

The following pairs of values of the refractive indices were used in calculating the constants of the natural dispersion equation for ethyl acetoacetate :—

TABLE VIII. (a).

λ in microns.	n .	b_1 .	b_0 .
·6678	1·4209 ₅	$1·121_8 \times 10^{-2}$	·9932 ₆
·4472	1·4327 ₉		
·5876	1·4237 ₈	$1·119_6 \times 10^{-2}$	·9935 ₁
·4100	1·4370 ₇		
·5016	1·4282 ₅	$1·161_3 \times 10^{-2}$	·9914 ₄
·3861	1·4408 ₇		

The mean values of b_1 and b_0 are $1·134_1 \times 10^{-2}$ and $·9927_4$ respectively, and the natural dispersion equation for ethyl acetoacetate at $10·4^\circ \text{C}$. is

$$n^2 = 1·9927 + \frac{1·134 \times 10^{-2}}{\lambda^2 - (\cdot 1089)^2}.$$

Table VIII. (b) contains a comparison of the observed results at certain wave-lengths and the values calculated from the above equation.

TABLE VIII. (b).

λ in microns.	n (observed).	n (calculated).
·5782	1·4242 ₇	1·4240 ₅
·4922	1·4288 ₇	1·4289 ₈
·4866	1·4293 ₂	1·4293 ₉
·4713	1·4304 ₄	1·4306 ₂
·4378	1·4338 ₄	1·4338 ₂
·4201	1·4358 ₇	1·4358 ₄
·4004	1·4385 ₇	1·4384 ₅
·3735	1·4432 ₇	1·4427 ₈

Ethyl Oxalate.

The pairs of values of λ and n used in calculating the constants b_0 and b_1 of the natural dispersion equation are given below in Table IX. (a).

TABLE IX. (a).

λ in microns.	n .	b_1	b_0 .
·6678	1·4126 ₀		
·4178	1·4266 ₃	$1·033_5 \times 10^{-2}$	·9716 ₁
·5876	1·4152 ₇		
·3532	1·4364 ₃	$1·025_7 \times 10^{-2}$	·9721 ₉
·5016	1·4194 ₆		
·3413	1·4389 ₃	$1·030_2 \times 10^{-2}$	·9717 ₃
·4472	1·4235 ₆		
·3267	1·4427 ₃	$1·045_8 \times 10^{-2}$	·9708 ₃

The mean values are $b_1 = 1·033_8 \times 10^{-2}$ and $b_0 = ·9715_9$. The natural dispersion equation for ethyl oxalate at 9·5° C. is thus :—

$$n^2 = 1·9716 + \frac{1·034 \times 10^{-2}}{\lambda^2 - (\cdot 1105)^2}.$$

A comparison is given below in Table IX. (b) between the refractive indices calculated from the above formula at certain wave-lengths and the values obtained experimentally.

TABLE IX. (b).

λ (microns).	n (observed).	n (calculated).
·5153	1·4186 ₈	1·4185 ₉
·4866	1·4204 ₃	1·4204 ₃
·4587	1·4225 ₁	1·4225 ₈
·4275	1·4255 ₃	1·4255 ₈
·4067	1·4279 ₃	1·4279 ₆
·3861	1·4307 ₃	1·4307 ₇
·3600	1·4352 ₃	1·4351 ₅
·3468	1·4377 ₆	1·4377 ₉
·3351	1·4404 ₃	1·4404 ₄

CALCULATION OF $\frac{e}{m}$.

As pointed out in the Introduction, the value of $\frac{e}{m}$ can be obtained from the relation

$$\frac{e}{m} = -\frac{2C^2K}{b_1}.$$

The values of K given in this paper have been calculated when δ is expressed in minutes per cm. gauss and λ in microns. For the purpose of evaluating $\frac{e}{m}$ from the above equation the values of K must be calculated when δ is expressed in radians per cm. gauss and λ in cm.

The absolute values of K for propyl propionate, isobutyl acetate, ethyl acetoacetate, and ethyl oxalate are $1.515_2 \times 10^{-14}$, $1.562_3 \times 10^{-14}$, $1.650_5 \times 10^{-14}$, and $1.568_4 \times 10^{-14}$ respectively. The corresponding values of b_1 are $.910 \times 10^{-10}$, $.924 \times 10^{-10}$, 1.134×10^{-10} , and 1.034×10^{-10} . On substituting these in the above equation the calculated values of $\frac{e}{m}$ for propyl propionate, isobutyl acetate, ethyl acetoacetate, and ethyl oxalate are $.99_9 \times 10^7$, 1.015×10^7 , $.87_3 \times 10^7$, and $.91_0 \times 10^7$ e.m.u. respectively.

DISCUSSION OF RESULTS.

Examination of the experimental results shows that the magneto-optical dispersion of each liquid over the range of spectrum investigated can be represented by an equation of the type

$$n\delta = K \frac{\lambda^2}{\{\lambda^2 - \lambda_1^2\}^2}, \quad \dots \dots \dots (a)$$

which involves one absorption band of wave-length λ_1 , situated in the Schumann-Lyman region of the spectrum. The refractive indices of the liquids can also be represented within experimental error by an equation of the type

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2}, \quad \dots \dots \dots (b)$$

where λ_1 has the same value as deduced from the magneto-optical experiments. It is considered, however, that errors of 2 or 3 in the fourth place of decimals are possible in the determinations of the refractive indices, and, consequently, the simple dispersional equation (b) may not be adequate, when more accurate values of the refractive indices in the ultra-violet are available.

The values of the various constants occurring in equations (a) and (b) are collected in the following table:—

TABLE X. (a).

Liquid.	Molecular weight.	$K \times 10^3$.	λ_1 (in microns).	b_0 .	$b_1 \times 10^2$.	$e/m \times 10^7$.	Temp. in °C.
Normal propyl propionate ($C_6H_{12}O_2$).	116	5.20 ₉	.1088	.9187	.910	.99 ₉	16.6
Isobutyl acetate ($C_6H_{12}O_2$).							
Ethyl acetoacetate ($C_6H_{10}O_3$).	130	5.67 ₄	.1089	.9927	1.134	.87 ₃	10.4
Ethyl oxalate ($C_6H_{10}O_4$).							
	146	5.39 ₂	.1105	.9716	1.034	.91 ₀	9.5

Although the compounds investigated have different structural formulæ, it is noticeable that the calculated values of λ_1 , only show a comparatively small variation. Uniform variations in the values of the various constants are only to be expected when substances of the same type are examined.

The constants of propionic acid, of methyl and ethyl propionates have previously been determined in this laboratory *†, and the results, together with those of normal propyl propionate, are collected in Table X. (b).

When the values of the constants of methyl, ethyl, and propyl propionates are compared, it is found that they increase progressively with increasing molecular weight.

* Stephens and Evans, *loc. cit.*

† Jenkins and Evans, *Phil. Mag.* vol. xi. p. 377 (February 1931).

This is not true when propionic acid is also considered, except in the case of λ_1 , the wave-length of the absorption band in the ultra-violet.

The addition of CH_2 increases the wave-length of the absorption band by about $\cdot 0012$ microns, on the average. For all the substances examined in this investigation, the calculations based on the simple theory sketched in the introduction to this paper, lead to values of e/m which are far too low.

TABLE X. (b).

Liquid.	Molecular weight.	$K \times 10^3$.	λ_1 (in microns).	b_0 .	$b_1 \times 10^2$.	$e/m \times 10^7$.	Temp. in $^\circ \text{C}.$
Propionic acid ($\text{C}_2\text{H}_5\text{COOH}$). }	74	5.00 ₈	$\cdot 1051$	$\cdot 9042$	$\cdot 872$	1.00	13.0
Methyl propionate ($\text{C}_2\text{H}_5\text{COOCH}_3$). }	88	4.77 ₂	$\cdot 1066$	$\cdot 8717$	$\cdot 868$	$\cdot 96$	17.1
Ethyl propionate ($\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$). }	102	5.06 ₈	$\cdot 1075$	$\cdot 8918$	$\cdot 899$	$\cdot 99$	15.8
Normal propyl propionate ($\text{C}_2\text{H}_5\text{COOC}_3\text{H}_7$). }	116	5.20 ₉	$\cdot 1088$	$\cdot 9187$	$\cdot 910$	$\cdot 99_9$	16.6

SUMMARY OF RESULTS.

1. The magneto-optical and ordinary dispersion of normal propyl propionate, isobutyl acetate, ethyl acetate, and ethyl oxalate have been examined in the visible and ultra-violet regions of the spectrum.

2. The magneto-optical dispersion of each liquid can be represented over the range of spectrum examined by an equation of the type

$$n\delta = K \cdot \frac{\lambda^2}{(\lambda^2 - \lambda_1^2)^2},$$

where n is the refractive index of the liquid for wave-length λ , δ Verdet's Constant for the same wave-length, K a constant which varies from liquid to liquid, and λ_1 is the wave-length of the absorption band in the ultra-violet.

The values of λ_1 , for the liquids mentioned in (1), are $\cdot 1088\mu$, 1080μ , 1089μ , and $\cdot 1105\mu$ respectively.

3. The ordinary dispersion of each liquid over the range of spectrum examined can be represented, within experimental error, by an equation of the type

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where λ_1 is the wave-length of the absorption band calculated from the magneto-optical experiments. The values of the constants b_0 and b_1 have been determined for each liquid.

4. The value of e/m for each liquid has been calculated from the magneto-optical and ordinary dispersion results.

The values for the liquids mentioned in (1) are $\cdot 99 \times 10^7$, $1\cdot 01_5 \times 10^7$, $\cdot 87_3 \times 10^7$, and $\cdot 91 \times 10^7$ e.m.u. respectively.

LXXIV. *Note on the Slow Motion of Fluid.*

By W. R. DEAN, M.A., *Trinity College, Cambridge* *.

1. **I**N a recent paper† the writer has considered the slow two-dimensional motion of fluid in a straight channel into which a barrier projects normal to one of the walls, the motion of the fluid, apart from the disturbance caused by the projection, being one of uniform shear. The writer is much indebted to Prof. G. I. Taylor for suggesting, after the first paper was published, that the variation in the fluid pressure near the projection should be determined, and an estimate so made of the pressure that would be measured by a certain type of Pitot tube‡ near the boundary of a moving fluid. In the present paper this is attempted.

Since the method of the previous paper was not found convenient for the evaluation of the pressure-gradient, which depends on the third-order differential coefficients of the stream-function, a new method is used, and the typical biharmonic function is different. The choice of biharmonic function was suggested by the formula in the theory of elasticity for the displacement of a plane plate, clamped

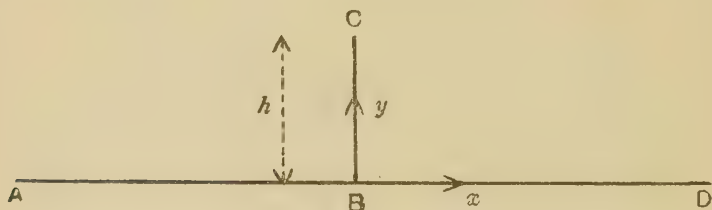
* Communicated by the Author.

† *Phil. Mag.* xiii. pp. 585-600 (1932).

‡ See below, § 6.

along a single straight edge, and acted upon by a concentrated transverse force. It is assumed that the projection is small, or (an equivalent assumption) that the influence of the second wall of the channel is negligible. The only boundary is therefore (see the figure) the wall AD and the projection BC. This restriction can be removed, but with difficulty, since there does not appear to be a formula in simple terms for the displacement of an elastic strip due to a concentrated force.

The method is necessarily approximate, but leads to results which are reliable except very near the end C of the projection; however, in spite of this exception, the difference in pressure between B and C can be found with some accuracy, the reason being that C can, in effect, be avoided since the pressure at any point on BC produced is the same as it is at C. This pressure-difference is the result required; it is found to be in good agreement with experiment.



2. It is required to find a stream-function ψ which satisfies the biharmonic equation

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)^2 \psi \equiv \nabla_1^4 \psi = 0, \quad . . . \quad (1)$$

and the boundary conditions

$$\psi = \frac{\partial \psi}{\partial \nu} = 0, \quad \quad (2)$$

on ABCD, $\frac{\partial}{\partial \nu}$ denoting, as usual, differentiation with respect to distance measured normal to the boundary. The stream-function must, further, be such as to give a motion of uniform shear at great distance from AD. Let

$$\psi = -\frac{1}{2}y^2 + \phi; \quad \quad (3)$$

then we must have

$$\nabla_1^4 \phi = 0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\phi = \frac{\partial \phi}{\partial y} = 0, \quad y = 0, \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\frac{\partial \phi}{\partial x} = 0, \quad \left\{ \begin{array}{l} x = 0, \quad 0 \leq y \leq 1. \end{array} \right\} \quad . \quad . \quad . \quad . \quad (6)$$

$$\phi = \frac{1}{2}y^2, \quad \left\{ \begin{array}{l} . \quad . \quad . \quad . \end{array} \right\} \quad (7)$$

Equations (3) to (7) are the non-dimensional forms of the equations for ψ and ϕ .

We can now make use of the solution of a somewhat similar problem in elasticity. Let a transverse force act at a point O of an infinite plane plate bounded by a single straight edge along which it is clamped. Then the displacement of any point P of the plate is proportional to *

$$-R^2 \log (R'/R) + (R'^2 - R^2)/2, \quad . \quad . \quad . \quad (8)$$

where R denotes the distance OP and R' the distance from P to O', the optical image of O in the straight edge. This function is biharmonic, vanishes together with its normal derivative at the straight edge, and is evidently symmetrical about a line through O perpendicular to the straight edge. Corresponding to any point O of the line BC in the figure, we therefore have a function which satisfies all except the last, (7), of the conditions imposed on ϕ , and by a suitable combination of these functions the last condition can be approximately satisfied. In terms of elasticity, the problem is now this: a plane plate clamped along AD is bent by flexural couples applied uniformly along another straight edge parallel to, and at great distance from, AD; to find what transverse forces must be applied to the points of BC if these points are to lie in the plane in which the plate is clamped. An exact solution obviously presents difficulty, but we can approximate by supposing that n forces act at C and at the $(n-1)$ points of BC whose distances from C are $1/n$, $2/n$, and so on, the forces being of such magnitudes that these n points lie in the required plane. This procedure applied to the problem of fluid motion with the values 8 and 10 of n appears to give a reliable result.

* A. E. H. Love, 'Mathematical Theory of Elasticity' (3rd Edition), § 314 (b).

3. Let $f_p(x, y)$ denote the function (8) when O, O' are the points $(0, \pm p/n)$. Then coefficients $A_1, A_2, \dots A_n$ must be found such that when $x=0$,

$$\sum_{p=1}^n A_p f_p(x, y) = \frac{1}{2}y^2, \quad y = \frac{1}{n}, \frac{2}{n}, \dots 1. \quad (9)$$

This requires that

$$\frac{q^2}{2n^2} = \sum_{p=1}^n A_p \left[\frac{2pq}{n^2} - \frac{(p-q)^2}{n^2} \log \left| \frac{p+q}{p-q} \right| \right], \quad q=1, 2, \dots n,$$

or, if

$$A_p' = pA_p,$$

that

$$\frac{q}{4} = \sum_{p=1}^n A_p' \left[1 - \frac{(p-q)^2}{2pq} \log \left| \frac{p+q}{p-q} \right| \right], \quad q=1, 2, \dots n, \quad (10)$$

the second term in the bracket being zero when p and q are equal.

This last form of the equations shows why, although the functions associated with points near C are clearly the most important, equally spaced points were taken on BC; the arithmetic is simplified in this way, since an increase in the value of n introduces new terms but does not alter the coefficients of the old terms.

The function

$$\phi = \sum_{p=1}^n \frac{1}{p} A_p' f_p(x, y), \quad (11)$$

obtained in this way satisfies conditions (4) to (6), but does not completely satisfy (7), since it equals $y^2/2$ only at the n selected points on BC and not for all values of y between 0 and 1. With a given value of n the accuracy of the result can, however, be tested by finding the difference between ϕ and $y^2/2$ at points of BC other than the selected points. This is the method adopted in the cases numerically considered, in default of a general proof that the process is convergent.

4. The values of the coefficients $A_1', A_2', \dots$ in the two cases $n=8, 10$, which have been examined in detail are tabulated below.

	$n=8.$	$n=10.$		$n=8.$	$n=10.$
A_1'	·0015	·0021	A_6'	— ·1473	— ·1555
A_2'	— ·0094	— ·0031	A_7'	— 3·3900	— ·3508
A_3'	— ·0391	— ·0191	A_8'	5·7174	— ·2153
A_4'	— ·0861	— ·0462	A_9'	—	— 4·8566
A_5'	— ·2214	— ·0904	A_{10}'	—	8·0233

Substitution of these values in (11) gives two approximations to the stream-function; the values for some points on the line BC are tabulated below.

$y.$	$\phi.$		$\psi(=-\frac{1}{2}y^2+\phi)$	
	$n=8.$	$n=10.$	$n=8.$	$n=10.$
·85	—	·36100	—	— ·00025
·9375	·44286	—	·00341	—
·95	—	·45369	—	·00244
1·1	·56515	·56624	— ·03985	— ·03876
1·2	·6147	·6163	— ·1053	— ·1037
1·5	·7202	·7232	— ·4048	— ·4018
2·0	·8279	·8321	— 1·1721	— 1·1679
3·0	·9434	·9484	— 3·5566	— 3·5516
5·0	1·045	1·051	— 11·455	— 11·449
10·0	1·128	1·135	— 48·871	— 48·865

The values of ψ given in the last two columns show a close agreement between the two approximations except in the immediate neighbourhood of the end of the projection. The stream-function should vanish for all values of y less than unity; when $n=10$, ψ vanishes for the values 0·9 and 1·0 of y , and mid-way between these values, at $y=0·95$, we may expect the largest error; this is found to be 0·00244, the error when y is 0·85 being ten times smaller. In case $n=8$, the greatest error will be roughly the value of ψ when $y=15/16$; this is 0·00341. This is enough to show, if the problem is considered from the point of view of the theory of elasticity, that the errors will be negligible apart from what is usually known as the "edge effect."

The best available test of the validity of either approximation near the projection consists in a comparison of the two values of the gradient $\partial\phi/\partial y$ at $y=1$; these values are 0·8090 and 0·8292 when $n=8, 10$, respectively, and differ by less than 3 per cent. There is a larger percentage

difference between the corresponding values, 0.1910 and 0.1708, of the gradient of ψ . We find in these values, as in the previous paper *, some evidence of a finite velocity of slip at the end of the projection. The gradients are, of course, calculated from the non-dimensional equations; if it is now supposed that the projection is of height h and that the velocity of the fluid is V at points where x is large and $y=h$, the velocities of slip are 0.1910 V and 0.1708 V . Although there is a rather large difference between these values, a reasonable conclusion seems to be that the velocity of slip is certainly finite (it would be infinite if viscosity were ignored) and probably different from zero.

However, the method of this paper, though more suitable than that of the last (since gradients and values of the stream-function are now known with the same accuracy), is hardly appropriate to decide the question.

5. The pressure is determined by the usual equations

$$\frac{\partial p}{\partial x} = \mu \nabla_1^2 u = -\mu \frac{\partial}{\partial y} \nabla_1^2 \psi,$$

$$\frac{\partial p}{\partial y} = \mu \nabla_1^2 v = \mu \frac{\partial}{\partial x} \nabla_1^2 \psi.$$

Since $\nabla_1^2 \psi$ is plane harmonic, we have, writing ξ for $\nabla_1^2 \psi$

$$\zeta \equiv \xi + i\eta = f(x + iy),$$

and may write the equations for the pressure in the form

$$\frac{\partial}{\partial x} [p - \mu\eta] = \frac{\partial}{\partial y} [p - \mu\eta] = 0.$$

It follows that

$$p = \mu\eta,$$

if an arbitrary constant is ignored.

We can now calculate the difference in pressure between two points which are near B but on opposite sides of the projection. Each term in ψ , with the evident exception of $-\frac{1}{2}y^2$, contributes to the difference. Consider the typical term

$$\psi = -R^2 \log(R/R') + (R'^2 - R^2)/2,$$

where R is measured from some point $(0, a)$ of BC. This gives

$$\nabla_1^2 \psi = \xi = 4 \log(R/R') + \frac{8a(y+a)}{x^2 + (y+a)^2},$$

* *Loc. cit.* p. 598.

whence

$$\zeta = 4 \log \frac{z - ai}{z + ai} + \frac{8ai}{z + ai}.$$

When a closed curve, surrounding $(0, a)$ but not $(0, -a)$, is described clockwise η decreases by 8π ; the corresponding decrease in pressure is $8\pi\mu$. Since this is independent of a , the pressure difference is obtained by multiplying by $8\pi\mu$ the sum of the coefficients $A_1, A_2, \dots$ of equations (9). The pressure near B on the left of BC is therefore greater than it is at the corresponding point on the right by

$$8\pi\mu [A_1' + \frac{1}{2}A_2' + \dots],$$

the general motion of the fluid being from left to right. In cases $n=8, 10$, the expression above gives pressure differences of $8\pi\mu$ (.1238) and $8\pi\mu$ (.1242), respectively. It will be seen that there is a close agreement between these values; the reason is that in calculating the pressure difference it is possible to take a path which keeps clear of the end of the projection.

The coefficient of $8\pi\mu$ is derived from equations in non-dimensional form, and applies when the height of the projection and the undisturbed velocity at its end are both unity; if units are now altered so that the height becomes h and the corresponding velocity V , there results for the pressure difference

$$0.124 \frac{8\pi\mu V}{h}, \dots \dots \dots (12)$$

approximately.

6. The calculation of the variation in pressure has an application to some experimental work undertaken by the late Sir T. E. Stanton and others* to examine the velocity-distribution of a fluid moving in the neighbourhood of a fixed boundary. The work was intended primarily to find whether there was an appreciable velocity of slip at the boundary of a fluid in turbulent motion, and whether there was near the boundary a narrow region in which the flow was laminar, and it was therefore essential to carry the exploration of the flow as near to the bounding wall as possible. When it was found that a small Pitot tube of the ordinary type was not effective, a modified Pitot tube was used, the orifice being rectangular and one side of the rectangle being formed by the bounding wall itself. The orifice was very small, the breadth was 1.27 mm.

* T. E. Stanton, D. Marshall, and C. N. Bryant, "On the Conditions at the Boundary of a Fluid in Turbulent Motion," Proc. Royal Soc. (A), xcvi. pp. 413-434 (1920).

and the depth variable but always considerably smaller than the breadth, so that, assuming the existence of a boundary layer of laminar flow, the experimental conditions were not unlike those assumed in the present paper. As it was not to be expected that the measured excess pressure would be $\frac{1}{2}\rho v^2$, v being the velocity at the centre of the orifice, the tube was calibrated and in terms of the depth d of the opening an "effective depth" d' was defined as the distance from the wall at which the velocity was v , $\frac{1}{2}\rho v^2$ being the measured pressure.

It was observed that the effective depth d' did not decrease to zero with the actual depth d of the orifice, and this was the subject of further experimental and theoretical work by Miss M. Barker*. Observing that with a low velocity the pressure measured by a Pitot tube would be proportional to v and not v^2 , this author assumed that the pressure corresponding to an opening of depth d was the pressure at the nose of a sphere of diameter d , the latter pressure being calculated by Stokes's formula for the velocity at the centre of the opening. The effective depth could be calculated on this assumption, and it was found that the limiting value as d decreased to zero was given by

$$d' = (3\mu/\rho\alpha)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where α denotes the rate of shear at the boundary. The limiting values so calculated were found to be in good agreement with the observed.

From the formula (12) for the change in pressure around the projection an upper limit for the effective depth d' can be calculated. One-half of (12) is the pressure difference between the points B and C; this is

$$1.56\mu V/h,$$

and must exceed the pressure that would be measured by a Pitot tube of the kind used by Stanton. According to definition d' is given by the equations

$$Vd'/h = \alpha d' = v, \quad \rho v^2/2 = 1.56\mu V/h,$$

whence

$$d' = (3.12\mu/\rho\alpha)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

It is curious that this result should be so close to (13); it leads, however, as it should, to values of d' greater than those observed, for the latter are somewhat smaller than those given by (13), especially when the velocity is small.

* Proc. Royal Soc. (A), ci. pp. 435-445 (1922).

LXXV. *On the Solution of Problems in Heat-conduction by the Method of Wave-trains.* By JAMES ROBERTSON, M.A., B.Sc., Lecturer in Mathematics at Jordanhill Training College, Glasgow*.

IN a series of papers† under a similar title Dr. G. Green has indicated a special method of solving problems in heat conduction. Each problem is regarded as one of wave-motion, so that we have available as an aid to its solution all the principles usually applied to such forms of motion. The usual procedure is to begin by considering the wave-train set up by a periodic source $\theta_0 \cos kt$ existing at some point within or on a boundary of the conducting medium. This train on arrival at any other boundary gives rise to a reflected and, it may be, a transmitted train. These are always perfectly determinate, if the permanent conditions at the reflecting surface are known. Following up the reflected train we may find that it is again reflected at other boundaries according to definite laws. Clearly this process goes on indefinitely. The problem of finding the temperature at any point due to the given periodic source is that of obtaining the resultant effect of the initial train and all the other trains set up by multiple reflexions at the various boundaries. In this way we find a solution of the fundamental differential equation of heat conduction already adapted to the various boundary conditions. To obtain from this result the effect due to an initial instantaneous temperature θ_0 we perform an integration with regard to k , and finally to obtain the effect due to a permanent temperature θ_0 we perform an integration with regard to t . The method for simple cases is as good as others, and has the advantage that it enables us to obtain solutions in cases where the boundary conditions are more complicated, where, in fact, they represent more probably those obtaining in practical laboratory work. The usefulness of the method when applied to problems where we have two media in contact will also be specially noticed.

In his papers Dr. Green has dealt with linear, spherical, and cylindrical problems and has obtained solutions for a great variety of cases. More commonly the initial temperature throughout the medium is prescribed and solutions are

* Communicated by George Green, D.Sc., Applied Physics Department, The University of Glasgow.

† *Phil. Mag.* iii. Suppl. (April 1927); v. (April 1928); ix. (Feb. 1930); xii. Suppl. (Aug. 1931).

obtained corresponding to various boundary conditions. The object of the present investigation is to apply the method to cases where a permanent temperature is maintained at one boundary*, the initial temperature of the medium being zero, various conditions applying at the other boundaries. For the present we confine our attention to linear flow; but it is hoped to communicate the spherical and cylindrical analogues later.

For purposes of reference we give a list of the actual problems solved.

- (i.) Rod of length a , end $x=0$ kept at a constant temperature θ_0 †, and end $x=a$ at temperature zero.
- (ii.) Same problem, but end $x=a$ rendered impervious to heat.
- (iii.) Semi-infinite rod, from $x=0$ to $x=a$ of conductivity K_1 , from $x=a$ to $x=\infty$ of conductivity K_2 . End $x=0$ kept at constant temperature θ_0 .
- (iv.) Rod of length a , end $x=0$ at constant temperature θ_0 . At end $x=a$ radiation taking place into a medium at temperature zero.
- (v.) Application to certain experimental methods of determining conductivity.
- (vi.) Rod of two materials, $x=0$ to $x=a$ of conductivity K_1 , $x=a$ to $x=b$ of conductivity K_2 : end $x=a$ kept at constant temperature θ_0 . End $x=b$ kept at temperature zero.
- (vii.) Same problem, but radiation at end $x=b$ into a medium at temperature zero.

§ 1. In every case we begin by supposing that at the end $x=0$ there is a periodic temperature source $\theta_0 \cos kt$. This may be regarded as setting up the positively travelling wave-train ‡

$$\theta_0 e^{-x\sqrt{\frac{k}{2\kappa}}} \cos \left\{ kt - x\sqrt{\frac{k}{2\kappa}} \right\}.$$

When this train arrives at the boundary $x=a$, it is reflected, the reflected negatively travelling wave being

$$A\theta_0 e^{-(2a-x)\sqrt{\frac{k}{2\kappa}}} \cos \left\{ kt - (2a-x)\sqrt{\frac{k}{2\kappa}} \right\},$$

* Green, *ibid.* 4th paper, p. 255.

† The solutions for the case $v=\phi(t)$, $x=0$ can be deduced from the solutions here obtained by a general method (see, e.g., Carslaw, 'Conduction of Heat,' p. 17 (1921)).

‡ The notation throughout is that used by Green.

from which we notice that at $x=a$, the phases of the incident and reflected waves are equal; also A will be chosen so that the permanent condition at $x=a$, violated on the arrival of the incident train, may be fulfilled. Following up the reflected train to $x=0$, we find that there a new positive train,

$$-A\theta_0 e^{-(2a+x)} \sqrt{\frac{k}{2\kappa}} \cos \left\{ kt - (2a+x) \sqrt{\frac{k}{2\kappa}} \right\},$$

is set up by reflexion. Notice that the permanent condition at $x=0$ has been maintained. Next we follow up this last train to the boundary $x=a$, where on arrival a further reflected train is set up. We represent this by

$$-A^2\theta_0 e^{-(4a-x)} \sqrt{\frac{k}{2\kappa}} \cos \left\{ kt - (4a-x) \sqrt{\frac{k}{2\kappa}} \right\}.$$

Clearly the process continues indefinitely. We proceed next to the summation at any point of the effects due to all these trains.

For the first of the problems listed above it is easy to see by considering any incident train and the corresponding reflected train, that $A=-1$. Thus if v' is the temperature at any point due to the periodic source $\theta_0 \cos kt$ at $x=0$,

$$v' = \theta_0 \sum_0^{\infty} e^{-(2na+x)} \sqrt{\frac{k}{2\kappa}} \cos \left\{ kt - (2na+x) \sqrt{\frac{k}{2\kappa}} \right\} \\ - \theta_0 \sum_1^{\infty} e^{-(2na-x)} \sqrt{\frac{k}{2\kappa}} \cos \left\{ kt - (2na-x) \sqrt{\frac{k}{2\kappa}} \right\}, \quad (1)$$

where we have summed separately the positively and the negatively travelling trains.

To obtain the effect v_1 due to the creation of the initial instantaneous temperature θ_0 at $x=0$, we have

$$v_1 = \frac{1}{\pi} \int_0^{\infty} v' dk. \quad (2)$$

For this purpose we require the fundamental result *

$$\frac{\theta_0}{\pi} \int_0^{\infty} e^{-x\sqrt{\frac{k}{2\kappa}}} \cos \left(kt - x \sqrt{\frac{k}{2\kappa}} \right) dk = \frac{\theta_0 x e^{-\frac{x^2}{4\kappa t}}}{2\sqrt{\pi\kappa t^3}}. \quad (3)$$

Applying the process indicated by (2) to (1), we obtain

$$v_1 = \frac{\theta_0}{2\sqrt{\pi\kappa t^3}} \sum_{-\infty}^{\infty} (2na+x) e^{-\frac{(2na+x)^2}{4\kappa t}}. \quad (4)$$

* Green, First paper, p. 787.

This result may be transformed by means of a well-known theorem*. Using the transformation, (4) becomes

$$\begin{aligned} v_1 &= \frac{\theta_0}{a\sqrt{\pi\kappa t^3}} \sum_1^\infty \sin \frac{n\pi x}{a} \int_0^\infty x' e^{-\frac{x'^2}{4\kappa t}} \sin \frac{n\pi x'}{a} dx' \\ &= \frac{2\pi\kappa\theta_0}{a^2} \sum_1^\infty n \sin \frac{n\pi x}{a} e^{-\frac{\kappa n^2 \pi^2 t}{a^2}} \dots \dots \dots (5) \end{aligned}$$

Finally, to obtain the effect V due to the permanent temperature θ_0 at $x=0$, we replace t in (5) by $(t-t')$ and integrate with regard to t' between the limits 0 and t . In this way we obtain

$$V = \frac{2\theta_0}{\pi} \sum_1^\infty \frac{1}{n} \sin \frac{n\pi x}{a} \left(1 - e^{-\frac{\kappa n^2 \pi^2 t}{a^2}}\right) \dots \dots \dots (6)$$

$$= \theta_0 \left(1 - \frac{x}{a}\right) - \frac{2\theta_0}{\pi} \sum_1^\infty \frac{1}{n} \sin \frac{n\pi x}{a} e^{-\frac{\kappa n^2 \pi^2 t}{a^2}}, \dots \dots (7)$$

where we have availed ourselves of a well-known sine series.

§ 2. If the end $x=a$ is rendered impervious to heat, the other conditions remaining the same, we have at $x=a$, $\frac{\partial v}{\partial x} = 0$. Clearly for this case $A=1$. With the same notation as before we obtain

$$\begin{aligned} v &= \theta_0 \sum_0^\infty (-1)^n e^{-\frac{(2na+x)^2}{4\kappa t}} \sqrt{\frac{k}{2\kappa}} \cos \left\{ kt - (2na+x) \sqrt{\frac{k}{2\kappa}} \right\} \\ &\quad - \theta_0 \sum_1^\infty (-1)^n e^{-\frac{(2na-x)^2}{4\kappa t}} \sqrt{\frac{k}{2\kappa}} \cos \left\{ kt - (2na-x) \sqrt{\frac{k}{2\kappa}} \right\}. \end{aligned} \dots \dots (8)$$

From this the k integration gives

$$\begin{aligned} v_1 &= \frac{\theta_0}{2\sqrt{\pi\kappa t^3}} \left\{ \sum_0^\infty (-1)^n (2na+x) e^{-\frac{(2na+x)^2}{4\kappa t}} \right. \\ &\quad \left. - \sum_1^\infty (-1)^n (2na-x) e^{-\frac{(2na-x)^2}{4\kappa t}} \right\} \dots \dots (9) \end{aligned}$$

$$\begin{aligned} &= \frac{\theta_0}{\sqrt{\pi\kappa t^3}} \sum_1^\infty \sin \frac{(2n-1)\pi x}{2a} \int_0^\infty x' e^{-\frac{x'^2}{4\kappa t}} \sin \frac{(2n-1)\pi x'}{2a} dx' \\ &= \frac{\pi\kappa\theta_0}{a^2} \sum_1^\infty (2n-1) \sin \frac{(2n-1)\pi x}{2a} e^{-\frac{\kappa(2n-1)^2 \pi^2 t}{4a^2}}, \dots \dots (10) \end{aligned}$$

* See, e. g., Carslaw, *ibid.* p. 159.

where we have used a transformation similar to that employed with (4) above. Proceeding next with the time integration, we find for the case of the permanent temperature θ_0 at $x=0$,

$$V = \frac{4\theta_0}{\pi} \sum_{n=1}^{\infty} \frac{1}{2n-1} \sin \frac{(2n-1)\pi x}{2a} \left\{ 1 - e^{-\frac{\kappa(2n-1)^2\pi^2 t}{4a^2}} \right\}$$

$$= \theta_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \sin \frac{(2n-1)\pi x}{2a} e^{-\frac{\kappa(2n-1)^2\pi^2 t}{4a^2}} \right\}, \quad (11)$$

in which we have used a well-known series for $\pi/4$.

Before proceeding with the next problem we indicate briefly the alternative method available for such cases as the above. It consists essentially in summing the series in (1) and (8) before carrying out the k integrations. We take as starting-point the periodic source $\theta_0 e^{ikt}$ at the origin. Then the initial train and the various reflected trains are

$$\begin{aligned} & \theta_0 e^{ikt+ix\lambda}, & A\theta_0 e^{ikt+i(2a-x)\lambda}, \\ & -A\theta_0 e^{ikt+i(2a+x)\lambda}, & -A^2\theta_0 e^{ikt+i(4a-x)\lambda}, \\ & +A^2\theta_0 e^{ikt+i(4a+x)\lambda}, & + \text{etc., etc.,} \end{aligned}$$

where $\sqrt{\frac{ik}{\kappa}} = i\lambda$ and $\sqrt{i} = e^{\frac{i5\pi}{4}}$.

Performing the summations, we find

$$v' = \theta_0 e^{-\kappa\lambda^2 t} \frac{e^{ix\lambda} + A e^{i(2a-x)\lambda}}{1 + A e^{i2a\lambda}} \dots \dots \dots (12)$$

Further, the integration indicated by (2) now becomes

$$v_1 = \frac{\kappa i \theta_0}{\pi} \int_C e^{-\kappa\lambda^2 t} \frac{e^{ix\lambda} + A e^{i(2a-x)\lambda}}{1 + A e^{i2a\lambda}} \lambda d\lambda, \quad \dots (13)$$

where the contour of integration C is the standard one for heat-conduction problems*. It consists of a curve in the

λ -plane joining the points $Re^{\frac{i\pi}{4}}$, $Re^{\frac{3i\pi}{4}}$, the curve approaching the lines $y = \pm x$ asymptotically from above ($\lambda = x + iy$). The evaluation of the integral (13)—which we regard as fundamental—for the various possible forms of A will receive

* Carslaw, *ibid.* p. 173.

some considerable attention. For example, with $A = -1$, as in the first problem above, we get, instead of (13),

$$v_1 = \frac{\kappa i \theta_0}{\pi} \int_C e^{-\kappa \lambda 2t} \frac{\sin(a-x)\lambda}{\sin a\lambda} \lambda d\lambda. \quad (14)$$

The integrand is an odd function having singularities at the roots of the equation $\sin a\lambda = 0$. In order to apply the residue theorem we take as closed contour the standard path C , its image in the real axis and circular arcs joining the ends of these curves at infinity. When the integral is evaluated in this way we obtain the result (5). Similarly, when $A = 1$, as in our second problem, the integral in (13) takes a form like that in (14), the sines being replaced by the corresponding cosines.

§ 3. The semi-infinite rod. Surface of separation at $x = a$ of two media of conductivities K_1, K_2 respectively. If v_1, K_1, κ_1 , etc., refer to the region $0 \leq x \leq a$, v_2, K_2, κ_2 , etc., to the region $x \geq a$, we have, at $x = a$,

$$v_1 = v_2; \quad K_1 \frac{\partial v_1}{\partial x} = K_2 \frac{\partial v_2}{\partial x} \quad (15)$$

Beginning again with a positive train emanating from a periodic source $\theta_0 \cos kt$ at $x = 0$, we take for this train, for its first reflected continuation within the first medium and for its transmitted continuation in the second, the following in order :

$$\begin{aligned} & \theta_0 e^{-x} \sqrt{\frac{k}{2\kappa_1}} \cos \left(kt - x \sqrt{\frac{k}{2\kappa_1}} \right), \\ & A \theta_0 e^{-(2a-x)} \sqrt{\frac{k}{2\kappa_1}} \cos \left\{ kt - (2a-x) \sqrt{\frac{k}{2\kappa_1}} \right\}, \\ & A' \theta_0 e^{-\dots} \cos \left\{ kt - \left[x - a \left(1 - \sqrt{\frac{\kappa_2}{\kappa_1}} \right) \right] \sqrt{\frac{k}{2\kappa_2}} \right\}, \end{aligned}$$

in which the omitted index—as in (18)—is easily inferred from an examination of the cosine factor.

The last of these goes on to infinity and never returns. The second arrives at the origin, is reflected there, setting up a new positive train which in turn, on arrival at $x = a$, is partly reflected and partly transmitted—the process continuing in this way indefinitely. The coefficients A and A'

are obtained by taking into account the conditions expressed by (15). Thus

$$A = \frac{K_1 \sqrt{\kappa_2} - K_2 \sqrt{\kappa_1}}{K_1 \sqrt{\kappa_2} + K_2 \sqrt{\kappa_1}}; \quad A' = \frac{2K_1 \sqrt{\kappa_2}}{K_1 \sqrt{\kappa_2} + K_2 \sqrt{\kappa_1}}. \quad (16)$$

For this case then, we find

$$v_1' = \theta_0 \left\{ \sum_0^{\infty} (-1)^n A^n e^{-(2na+x)} \sqrt{\frac{k}{2\kappa_1}} \cos \left(kt - \overline{2na} + x \sqrt{\frac{k}{2\kappa_1}} \right) \right. \\ \left. - \sum_1^{\infty} (-1)^n A^n e^{-(2na-x)} \sqrt{\frac{k}{2\kappa_1}} \cos \left(kt - \overline{2na} - x \sqrt{\frac{k}{2\kappa_1}} \right) \right\}, \quad (17)$$

$$v_2' = A' \theta_0 \sum_0^{\infty} (-1)^n A^n e^{-\dots} \\ \times \cos \left\{ kt - \left[x - a \left(1 - \overline{2n} + 1 \sqrt{\frac{\kappa_2}{\kappa_1}} \right) \right] \sqrt{\frac{k}{2\kappa_2}} \right\}. \quad (18)$$

The usual integration with regard to k gives

$$v_1 = \frac{\theta_0}{2\sqrt{\pi\kappa_1}t^{\frac{3}{2}}} \left\{ \sum_0^{\infty} (-1)^n A^n (2na+x) e^{-\frac{(2na+x)^2}{4\kappa_1 t}} \right. \\ \left. - \sum_1^{\infty} (-1)^n A^n (2na-x) e^{-\frac{(2na-x)^2}{4\kappa_1 t}} \right\}, \quad (19)$$

$$v_2 = \frac{A' \theta_0}{2\sqrt{\pi\kappa_2}t^{\frac{3}{2}}} \sum_0^{\infty} (-1)^n A^n \left\{ x - a \left(1 - \overline{2n} + 1 \sqrt{\frac{\kappa_2}{\kappa_1}} \right) \right\} e^{-\frac{(\dots)^2}{4\kappa_2 t}}. \quad (20)$$

Before proceeding with the time integration we take the verification of the last two results by the alternative contour integral method. We find that v_1 is given by (13) and v_2 by

$$v_2 = \frac{A' \kappa_1 i \theta_0}{\pi} \int_C e^{-\kappa_1 \lambda^2 t} \frac{e^{i\{a+\mu(x-a)\}\lambda}}{1 + A e^{i2a\lambda}} \lambda d\lambda, \quad (21)$$

where A, A' have the values stated in (16) and $\mu = \sqrt{\frac{\kappa_1}{\kappa_2}}$.

In the present case the roots of the equation $1 + A e^{i2a\lambda} = 0$ are given by

$$\lambda = \frac{(2n+1)\pi}{2a} - \frac{i}{2a} \log A,$$

so that, if A as defined is less than 1, the equation has no root in the upper half of the λ -plane. Hence, with the

vanishing of the integral over circular arcs at infinity, we get

$$\begin{aligned}
 v_1 &= -\frac{\kappa_1 i \theta_0}{\pi} \int_{-\infty}^{\infty} e^{-\kappa_1 \lambda^2 t} \frac{e^{i x \lambda} + A e^{i(2a-x)\lambda}}{1 + A e^{i 2 a \lambda}} - \lambda d\lambda \\
 &= \frac{2\kappa_1 \theta_0}{\pi} \int_0^{\infty} e^{-\kappa_1 \lambda^2 t} \frac{(1-A^2) \sin x \lambda}{1 + 2A \cos 2a\lambda + A^2} \lambda d\lambda \\
 &= \frac{2\kappa_1 \theta_0}{\pi} \int_0^{\infty} e^{-\kappa_1 \lambda^2 t} \left\{ \sin x \lambda + \sum_1^{\infty} (-1)^n A^n \right. \\
 &\quad \times [\sin (2na+x)\lambda - \sin (2na-x)\lambda] \left. \right\} \lambda d\lambda, \quad (22)
 \end{aligned}$$

where we have employed a well-known expansion. When we apply term by term integration to the right of (22) we obtain the result (19). In the same way from (21) we could obtain the result (20).

Now, proceeding with the usual time integration, we find from (19) and (20), after some reduction,

$$\begin{aligned}
 V_1 &= \frac{2\theta_0}{\sqrt{\pi}} \left\{ \frac{\sqrt{\pi}}{2} - \int_0^{\frac{x}{2\sqrt{\kappa_1 t}}} e^{-\alpha^2} d\alpha - \sum_1^{\infty} (-1)^n A^n \left(\int_{\frac{2na-x}{2\sqrt{\kappa_1 t}}}^{\frac{2na+x}{2\sqrt{\kappa_1 t}}} e^{-\alpha^2} d\alpha \right) \right\}; \\
 &\quad \dots \dots (23)
 \end{aligned}$$

also, noticing that $1+A=A'$, we obtain

$$V_2 = \frac{2A'\theta_0}{\sqrt{\pi}} \left\{ 2A' - \sum_0^{\infty} (-1)^n A^n \int_0^{\xi} e^{-\alpha^2} d\alpha \right\}, \quad (24)$$

where

$$\xi = \frac{x-a \left\{ 1 - (2n+1) \sqrt{\frac{\kappa_2}{\kappa_1}} \right\}}{2\sqrt{\kappa_2 t}}.$$

Verify that the solutions (23) and (24) do actually satisfy the conditions of the problem. At $x=a$, *e. g.*, (23) becomes

$$V_1 = \frac{2\theta_0}{\sqrt{\pi}} \left\{ \frac{\sqrt{\pi}}{2} - \int_0^{\frac{a}{2\sqrt{\kappa_1 t}}} e^{-\alpha^2} d\alpha - \sum_1^{\infty} (-1)^n A^n \left(\int_{\frac{(2n-1)a}{2\sqrt{\kappa_1 t}}}^{\frac{(2n+1)a}{2\sqrt{\kappa_1 t}}} e^{-\alpha^2} d\alpha \right) \right\},$$

and, by writing out in full a few terms of the summation, it will be seen that this result is equivalent to

$$V_1 = \frac{2\theta_0}{\sqrt{\pi}} \left\{ \frac{\sqrt{\pi}}{2} - (1+A) \sum_0^{\infty} (-1)^n A^n \int_0^{\frac{(2n+1)a}{2\sqrt{\kappa_1 t}}} e^{-\alpha^2} d\alpha \right\}.$$

Clearly from (24) this last result is just the form taken by V_2 at $x=a$.

Further,

$$\begin{aligned} \left(\frac{\partial V_1}{\partial x} \right)_a &= \frac{\theta_0}{\sqrt{\pi \kappa_1 t}} \left\{ -e^{-\frac{a^2}{4\kappa_1 t}} - \sum_1^{\infty} (-1)^n A^n \left(e^{-\frac{(2n+1)^2 a^2}{4\kappa_1 t}} + e^{-\frac{(2n-1)^2 a^2}{4\kappa_1 t}} \right) \right\} \\ &= \frac{\theta_0}{\sqrt{\pi \kappa_1 t}} \left\{ -(1-A) \sum_0^{\infty} (-1)^n A^n e^{-\frac{(2n+1)^2 a^2}{4\kappa_1 t}} \right\} \end{aligned}$$

and

$$\left(\frac{\partial V_2}{\partial x} \right)_a = \frac{A' \theta_0}{\sqrt{\pi \kappa_2 t}} \left\{ - \sum_0^{\infty} (-1)^n A^n e^{-\frac{(2n+1)^2 a^2}{4\kappa_1 t}} \right\}.$$

Clearly then,

$$\left(\frac{\partial V_1}{\partial x} \right)_a \div \left(\frac{\partial V_2}{\partial x} \right)_a = \frac{1-A}{A'} \sqrt{\frac{\kappa_2}{\kappa_1}} = \frac{K_2}{K_1},$$

as required.

In the remaining problems only the method leading to solutions in the form of contour integrals will be employed.

§ 4. Consider next the rod of length a , the end $x=0$ being kept at the uniform temperature θ_0 , while at the end $x=a$ there is radiation into a medium at constant temperature zero, i. e., at $x=a$, we have

$$-K \frac{\partial v}{\partial x} = hv. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The problem now is to evaluate the fundamental integral in (13) when A has the value appropriate to the condition (25). For this case A is given by

$$A = \frac{Ki\lambda - h}{Ki\lambda + h}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

so that if we write $\tan \phi$ for $K\lambda/h$, we find

$$v_1 = \frac{\kappa i \theta_0}{\pi} \int_C e^{-\kappa \lambda^2 t} \frac{\sin \{ \lambda(a-x) + \phi \}}{\sin(a\lambda + \phi)} \lambda d\lambda. \quad . \quad (27)$$

Carrying out the evaluation in the usual way we obtain

$$v_1 = 2\kappa\theta_0 \sum_1^{\infty} \frac{h^2 + K^2\lambda^2}{h(K + ah) + aK^2\lambda^2} \lambda \sin x\lambda e^{-\kappa\lambda^2 t},$$

where the summation is with respect to all the positive roots of the equation

$$\tan a\lambda = -\frac{K\lambda}{h}. \quad . \quad . \quad . \quad . \quad (28)$$

Finally, the time integration yields

$$V = 2\theta_0 \sum \frac{h^2 + K^2\lambda^2}{h(K + ah) + aK^2\lambda^2} \frac{\sin x\lambda}{\lambda} (1 - e^{-\kappa\lambda^2 t}). \quad (29)$$

This result can be exhibited in more usual form if we examine the limiting case $t \rightarrow \infty$. In this instance, as in others discussed below, it is possible to predict from the outset the "steady" temperature ultimately obtained. If this temperature—a function of x —be equated to the right of (29) when t is made infinite, we obtain a result susceptible of direct mathematical verification. Filling in the known "steady" temperature we get instead of (29),

$$V = \theta_0 \left\{ \frac{K + h(a-x)}{K + ah} - 2 \sum \frac{h^2 + K^2\lambda^2}{h(K + ah) + aK^2\lambda^2} \cdot \frac{\sin x\lambda}{\lambda} e^{-\kappa\lambda^2 t} \right\}. \quad . \quad . \quad . \quad (30)$$

This would seem to indicate the validity of the expansion

$$\frac{K + h(a-x)}{K + ah} = 2 \sum \frac{h^2 + K^2\lambda^2}{h(K + ah) + aK^2\lambda^2} \frac{\sin x\lambda}{\lambda},$$

the summation being with regard to all the positive roots of (28). The expansion is in fact correct*.

§ 5. The foregoing considerations, leading to results already well known, have been introduced merely to illustrate the possibilities of the method. It seems desirable as a useful application of the solutions obtained to consider the more complete theory of certain laboratory methods of measuring conductivity†. In the particular method contemplated we have a uniform rod, one end of which is kept at the constant temperature θ_0 . To the other end is soldered a copper ball

* Carslaw, *ibid.* p. 75.

† See, e. g., J. H. Gray, Proc. Roy. Soc. 1894. Methods based on that of Gray have been in use in the Physical Laboratory at Glasgow University for some time.

from the surface of which we may suppose there are heat losses according to the usual simple law. It is assumed that the whole of the ball at once takes the temperature of the end of the rod. Ordinarily a uniform temperature gradient along the bar is the basis for the calculations. The following treatment indicates how the simple theory might be modified.

We might represent the condition at the ball end of the rod by

$$-K\varpi \frac{\partial v}{\partial x} = M_s \frac{\partial v}{\partial t} + hSv, \quad \text{or say,} \quad -K \frac{\partial v}{\partial x} = q \frac{\partial v}{\partial t} + pv, \quad \dots \dots (31)$$

also $v = \theta_0$ at $x = 0$.

ϖ = sectional area of rod, M_s = thermal capacity of ball, S = surface area of ball.

First, for the effect of the instantaneous initial temperature θ_0 , we have to evaluate the fundamental integral in (13) for the particular value of A determined by (31). Again, by considering any incident train and its continuation by reflexion at $x = a$, we find

$$A = \frac{K\lambda + (p - q\kappa\lambda^2)}{K\lambda - (p - q\kappa\lambda^2)}. \quad \dots \dots (32)$$

Inserting this value in the integral and evaluating in the usual way, the result is

$$\begin{aligned} v' &= 2\theta_0 \sum \frac{K^2\lambda^2 + (p - q\kappa\lambda^2)^2}{a\{K^2\lambda^2 + (p - q\kappa\lambda^2)^2\} + K(p + q\kappa\lambda^2)} \lambda \sin x\lambda e^{-\kappa\lambda^2 t} \\ &\dots \dots (33) \\ &= 2\theta_0 \sum A_n \lambda \sin x\lambda e^{-\kappa\lambda^2 t}, \quad \text{say,} \end{aligned}$$

the summation being with respect to all the positive roots of the equation

$$\tan a\lambda = \frac{-K\lambda}{p - q\kappa\lambda^2}. \quad \dots \dots (34)$$

Finally, for the effect of the permanent temperature θ_0 at $x = 0$,

$$V = \theta_0 \left(1 - \frac{px}{K + pa}\right) - 2\theta_0 \sum A_n \frac{\sin x\lambda}{\lambda} e^{-\kappa\lambda^2 t}, \quad \dots (35)$$

where we have again availed ourselves of the device of filling in the first term on the right from considerations of the

"steady" temperature. The implication of the result (35) is that

$$\left(1 - \frac{px}{K + pa}\right) = \Sigma 2A_n \frac{\sin x\lambda}{\lambda}, \quad \dots \quad (36)$$

where A_n has the form indicated in (33) and where the summation is with regard to all the positive roots of (34). It seems desirable that this purely mathematical result be otherwise verified.

Assume that

$$f(x) = \Sigma A_n \sin \lambda_n x, \quad 0 \leq x \leq a,$$

then

$$\int_0^a f(x) \sin \lambda_m x \, dx = \Sigma \int_0^a A_n \sin \lambda_n x \sin \lambda_m x \, dx,$$

λ_m and λ_n being two of the roots of (34). It will be found that this last written integral has the value

$$-\frac{q\kappa}{K} \sin \lambda_m a \sin \lambda_n a,$$

except when $m = n$. Hence

$$\begin{aligned} \int_0^a f(x) \sin \lambda_m x \, dx &= -\frac{q\kappa}{K} \Sigma' A_n \sin \lambda_n a \sin \lambda_m a + \frac{A_m}{2} \left(a - \frac{\sin 2\lambda_m a}{2\lambda_m} \right) \\ &= -\frac{q\kappa}{K} \{ f(a) - A_m \sin \lambda_m a \} \sin \lambda_m a + \frac{A_m}{2} \left(a - \frac{\sin 2\lambda_m a}{2\lambda_m} \right). \end{aligned}$$

From this we have our method of obtaining the various coefficients A_m ,

$$A_m = \frac{\int_0^a f(x) \sin \lambda_m x \, dx + \frac{q\kappa}{K} \sin \lambda_m a f(a)}{\frac{q\kappa}{K} \sin^2 \lambda_m a + \frac{1}{2} \left(a - \frac{\sin 2\lambda_m a}{2\lambda_m} \right)}.$$

If we take for $f(x)$ the function on the left of (36) we obtain for A_m exactly the value required by (33).

To estimate the practical importance of the result (35) we must consider how many terms of the series need be retained, having regard to the numerical values of the various constants involved. For the sake of definiteness we make a brief arithmetical examination, taking values suggested by the apparatus used by Gray in the original investigation;

e. g., for an iron rod—selecting a relatively poor conductor, $K=0.167$, $\kappa=0.2016$, $a=6.28$; radius of rod 0.2; radius of copper ball 2.75; $h=0.0003$. With these values the equation (34) becomes

$$\tan 6.28 \lambda = -\frac{0.001358 \lambda}{0.001845 - \lambda^2}.$$

The roots of this equation are given approximately by

$$\lambda = 0.04534, 0.505, 1.000, 1.5, 2, \dots,$$

with corresponding values for $a\lambda$. Thus, if it is the intention to observe the temperature at $x=a$, i. e., the temperature of the ball—we see that for this value of x all the terms on the right of (35) after the third are practically zero. Thus

$$V_a = \theta_0 \left\{ \frac{K}{K+pa} - 2A_1 \frac{\sin a\lambda_1}{\lambda_1} e^{-\kappa\lambda_1^2 t} - 2A_2 \frac{\sin a\lambda_2}{\lambda_2} e^{-\kappa\lambda_2^2 t} \right\},$$

or numerically

$$V_a = \theta_0 \{ 0.1049 - 0.1069 e^{-0.0004145 t} + 0.00197 e^{-0.05052 t} \}.$$

This result incidentally gives some idea of the rapidity of the convergence of the series on the right of (36) when $x=a$, to the value of the function on the left, for the particular values of the constants chosen. Commenting further on this last result, since the unit of time is the second we see that for experimental work extending to minutes, except near the commencement of any experiment, the third term is relatively negligible. It would seem quite a justifiable conclusion, then, to take

$$V_a = \theta_0 \left\{ \frac{K}{K+pa} - A_1 e^{-\kappa\lambda_1^2 t} \right\} \dots \dots (36')$$

It is of interest to compare this result with that obtained by assuming—as in ordinary laboratory practice—a uniform temperature gradient along the bar. If in (31) we put

$(\theta_0 - v_a)/a$ for $-\frac{\partial v}{\partial x}$ and integrate this equation, we get

$$V_a = \frac{K\theta_0}{K+pa} \left\{ 1 - e^{-\frac{K+pa}{aq} t} \right\},$$

or numerically, with the same data as before,

$$V_a = \theta_0 (0.1049 - 0.1049 e^{-0.0004155 t}),$$

as compared with

$$V_a = \theta_0(0.1049 - 0.1069 e^{-0.0004145 t})$$

given by the present theory.

The conclusion reached in (36') would seem to indicate the following process for the determination of the constants K and h . Notice that $\theta_0 K / (K + p a)$, the steady temperature, can be observed directly or inferred from a temperature-time curve. Let the value be θ_0 / f . Then $p = K(f - 1)/a$. Next

$$\frac{\partial v}{\partial t} = \kappa \lambda_1^2 A_1 \theta_0 e^{-\kappa \lambda_1^2 t},$$

so that if we take the ratio g_1/g_2 of the values of $\frac{\partial v}{\partial t}$ at two instants t_1, t_2 we get

$$\kappa \lambda_1^2 = \frac{1}{t_2 - t_1} \log \frac{g_1}{g_2};$$

g_1 and g_2 may be obtained from the temperature-time curve, so that $\kappa \lambda_1^2$ is now determined. Finally, λ_1 is the smallest root of the equation

$$\tan a\lambda = \frac{-K\lambda}{p - q\kappa\lambda^2} = \frac{-c\rho\lambda}{c\rho(f-1) - q\lambda^2},$$

in which all the quantities are now known. The root may be obtained graphically and, since we know $\kappa \lambda_1^2$, κ can now be calculated. The constant h is obtained by putting the calculated value of κ in the formula $p = K(f - 1)/a$.

In view of possible applications of the theory given, it should be remembered that the conclusions reached apply only to apparatus of the particular design specified. For rods of different length and section and for a ball of greater or smaller surface area we would have to consider again the special form taken by the general result (35). The assumption also that the entire ball at once takes the temperature of the end of the rod would require further examination. In that respect the theory is still incomplete.

§ 6. One of the most striking successes of the wave-train method of building up the temperature at any point in a medium due to prescribed periodic heat sources has been fully demonstrated by Dr. Green in his third paper, where he considers the problem of flow of heat in a sphere of one material surrounded by a concentric sheath of another. At a surface $r = r_1$ in either medium a periodic surface source

ge^{ikt} is postulated, and by considering the various reflexions at the outer boundary, at the centre and at the surface of separation, of the original inwards and outwards trains, expressions for the temperature in either medium are obtained. From these, in the usual manner, the Green's Function for a particular type of boundary condition is obtained, and from this the temperature due to any arbitrary initial temperature distribution throughout the medium. We propose now to take up the corresponding one-dimensional problem. Instead of prescribing an initial temperature, however, we take this—as in the other problems of the present paper—to be zero, except that at $x=0$ we have the constant temperature θ_0 . The problem is fully represented by

$$\frac{\partial v_1}{\partial t} = \kappa_1 \frac{\partial^2 v}{\partial x^2}, \quad 0 \leq x \leq a, \quad \frac{\partial v_2}{\partial t} = \kappa_2 \frac{\partial^2 v_2}{\partial x^2}, \quad a \leq x \leq b,$$

$$v_1 = \theta_0, \quad x = 0; \quad v_1 = v_2 \quad \text{and} \quad K_1 \frac{\partial v_1}{\partial x} = K_2 \frac{\partial v_2}{\partial x}, \quad x = a.$$

The condition to be satisfied at $x=b$ may conveniently be specified later. As the process of building up the temperature at any point due to the source $\theta_0 e^{ikt}$ at $x=0$ resembles closely the analysis for the corresponding spherical case already fully given* we need not go into detail to the same extent. The first effect in medium 1, due to the original train and all the others set up by reflexion at $x=a$ and $x=0$ is

$$\theta_0 e^{ikt} \frac{e^{ix\lambda} + A e^{i(2a-x)\lambda}}{1 + A e^{i2a\lambda}},$$

where A is the coefficient for reflexion at the boundary $x=a$. Now regard all the positive elements of this effect as constituting a single positive train and consider the transmission of this train at $x=a$ into medium 2. By this train and its continuations by reflexion at $x=b$ and $x=a$ the primary effect in medium 2 is built up. It is

$$A' \theta_0 e^{ikt + ai\lambda} \frac{e^{\mu(x-a)i\lambda} + B e^{\mu\{2c-(x-a)\}i\lambda}}{(1 + A e^{2ai\lambda})(1 - B C' e^{2\mu ci\lambda})},$$

where A' is the coefficient for transmission from medium 1 to medium 2, B the coefficient for reflexion at $x=b$, C' the coefficient for internal reflexion in medium 2 at $x=a$; also

$$c = (b-a), \quad \mu = \sqrt{\frac{\kappa_1}{\kappa_2}}.$$

* Green, Phil. Mag. ix. p. 248 (Feb. 1930).

Next regard all the negative constituents of this last effect as combining to form a single negative train. This by transmission across $x=a$ and by its continuations by reflexion at $x=0$ and $x=a$ builds up the secondary effect in medium 1, viz.,

$$A'BC\theta_0 e^{ikt+2(a+\mu c)i\lambda} \frac{-e^{ix\lambda} + e^{-ix\lambda}}{(1 + Ae^{2ai\lambda})^2(1 - BC'e^{2\mu ci\lambda})},$$

where C is the coefficient for transmission from medium 2 to medium 1. In the same way, following up the positive part of this last effect across $x=a$ into medium 2 and treating it exactly as before, we obtain for the secondary effect in medium 2

$$-A'^2BC\theta_0 e^{ikt+(3a+2\mu c)i\lambda} \frac{e^{\mu(x-a)i\lambda} + B_{e\mu}\{2c-(x-a)\}i\lambda}{(1 + Ae^{2ai\lambda})^2(1 - BC'e^{2\mu ci\lambda})^2}.$$

Continuing the process by taking the negative part of this last effect, we next find the third effect in medium 1 as

$$A'^2B^2C^2\theta_0 e^{ikt+(4a+4\mu c)i\lambda} \frac{e^{ix\lambda} - e^{-ix\lambda}}{(1 + Ae^{2ai\lambda})^3(1 - BC'e^{2\mu ci\lambda})^2}.$$

Clearly the process goes on indefinitely. An examination of the forms of the first two effects in medium 2 shows that the various effects are given by the terms of a geometric progression. In the same way, if we re-write the first effect in medium 1 in the form

$$\theta_0 e^{ikt} \left\{ e^{-ix\lambda} + \frac{2i \sin x\lambda}{1 + Ae^{2ai\lambda}} \right\},$$

we see that, except for the first term, the various order effects in this medium are again given by the terms of a geometric progression. The sums are easily written down. For our present problem, then, we have first to consider the integrals

$$v_1 = \frac{\kappa i \theta_0}{\pi} \int_0^{\infty} e^{-\kappa \lambda^2 t} \left\{ e^{-ix\lambda} + \frac{2i \sin x\lambda (1 - BC'e^{2\mu ci\lambda})}{D} \right\} \lambda d\lambda, \quad \dots (37)$$

$$v_2 = \frac{\kappa i \theta_0}{\pi} \int_0^{\infty} e^{-\kappa \lambda^2 t} \frac{A'e^{ai\lambda} + B_{e\mu}\{2c-(x-a)\}i\lambda}{D} \lambda d\lambda, \quad \dots (38)$$

where

$$D = (1 + Ae^{2ai\lambda})(1 - BC'e^{2\mu ci\lambda}) + A'BCe^{2(a+\mu c)i\lambda}.$$

We proceed next to the evaluation of these integrals for the various forms of A , B , etc. If, *e.g.*, the end $x=b$ is kept at

zero temperature, we have $B = -1$. The values of A and A' are as in (16); also we find that

$$C' = -A, \quad C = 1 + C' = 1 - A, \quad A' = 1 + A.$$

In these circumstances we find that (37), after some reduction, takes the form

$$v_1 = \frac{\kappa i \theta_0}{\pi} \int_0^\infty e^{-\kappa \lambda^2 t} \frac{f_1(\lambda) \cos x\lambda + f_2(\lambda) \sin x\lambda}{f_1(\lambda)} \lambda d\lambda, \quad (39)$$

and (38) the form

$$v_2 = \frac{\sigma \kappa i \theta_0}{\pi} \int_0^\infty e^{-\kappa \lambda^2 t} \frac{\sin \mu(b-x)\lambda}{f_1(\lambda)} \lambda d\lambda, \quad (40)$$

where

$$f_1(\lambda) = \sin a\lambda \cos \mu c\lambda + \sigma \cos a\lambda \sin \mu c\lambda, \quad (41)$$

$$f_2(\lambda) = \sigma \sin a\lambda \sin \mu c\lambda - \cos a\lambda \cos \mu c\lambda, \quad (42)$$

$\sigma = K_1/\mu K_2$. The evaluations of the integrals are effected in the usual way. Proceeding at once to the usual time integration, we find that the required results are

$$\begin{aligned} V_1 &= -2\theta_0 \sum \frac{f_2(\lambda)}{f_1'(\lambda)} \frac{\sin x\lambda}{\lambda} (1 - e^{-\kappa \lambda^2 t}) \\ &= \theta_0 \left\{ 1 - \frac{K_2 x}{K_1(b-a) + K_2 a} \right\} + 2\theta_0 \sum \frac{f_2(\lambda)}{f_1'(\lambda)} \frac{\sin x\lambda}{\lambda} e^{-\kappa \lambda^2 t}, \end{aligned} \quad (43)$$

$$V_2 = \theta_0 \frac{K_1(b-x)}{K_1(b-a) + K_2 a} + 2\theta_0 \sum \frac{\sigma \sin \mu(b-x)\lambda}{f_1'(\lambda)} \frac{e^{-\kappa \lambda^2 t}}{\lambda}, \quad (44)$$

where the summations are with regard to all the positive roots of $f_1(\lambda) = 0$, and where again we have filled in the first terms from considerations of the steady state. Before taking up the verification of the purely mathematical results implied in (43) and (44), we rewrite these equations in a slightly different form. A full discussion of the roots of the equation

$$f_1(\lambda) = 0 \quad (45)$$

is given by Carslaw* in his discussion of what is virtually the same problem. Except in a very special case the equation is equivalent to

$$\cot \mu c\lambda + \sigma \cot a\lambda = 0, \quad (46)$$

* *Ibid.* p. 215.

so that (43) and (44) may now be rewritten

$$V_1 = \theta_0 \left\{ 1 - \frac{K_2 x}{K_1(b-a) + K_2 a} \right\} + 2\theta_0 \sum \frac{\sigma \operatorname{cosec}^2 a\lambda}{\frac{d}{d\lambda}(\sigma \cot a\lambda + \cot \mu c\lambda)} \frac{\sin x\lambda}{\lambda} e^{-\kappa\lambda^2 t}, \quad (47)$$

$$V_2 = \theta_0 \left\{ \frac{K_1(b-x)}{K_1(b-a) + K_2 a} \right\} + 2\theta_0 \sum \frac{\sigma \operatorname{cosec} a\lambda \operatorname{cosec} \mu c\lambda}{\frac{d}{d\lambda}(\sigma \cot a\lambda + \cot \mu c\lambda)} \frac{\sin \mu(b-x)\lambda}{\lambda} e^{-\kappa\lambda^2 t}. \quad (48)$$

We are therefore led to ask if the following type of expansion is possible:

$$F_1(x) = \sum A_m \sin \mu c\lambda_m \sin x\lambda_m, \quad 0 \leq x \leq a,$$

$$F_2(x) = \sum A_m \sin a\lambda_m \sin \mu(b-x)\lambda_m, \quad a \leq x \leq b,$$

the summations being with respect to all the positive roots of (46). Assuming the possibility of the expansion, we have

$$\sigma F_1(x) \sin \mu c\lambda_n \sin x\lambda_n = \sum \sigma A_m \sin \mu c\lambda_m \sin \mu c\lambda_n \sin x\lambda_m \sin x\lambda_n, \quad . \quad . \quad . \quad (49)$$

$$\mu F_2(x) \sin a\lambda_n \sin \mu(b-x)\lambda_n = \sum \mu A_m \sin a\lambda_m \sin a\lambda_n \sin \mu(b-x)\lambda_m \sin \mu(b-x)\lambda_n. \quad (50)$$

Now it can be seen that

$$\begin{aligned} & \sigma \sin \mu c\lambda_m \sin \mu c\lambda_n \int_0^a \sin x\lambda_m \sin x\lambda_n dx \\ & + \mu \sin a\lambda_m \sin a\lambda_n \int_a^b \sin \mu(b-x)\lambda_m \sin \mu(b-x)\lambda_n dx \\ & = \frac{\sin a\lambda_m \sin a\lambda_n \sin \mu c\lambda_m \sin \mu c\lambda_n}{\lambda_m^2 - \lambda_n^2} \\ & \quad \times \{ \lambda_n (\sigma \cot a\lambda_n + \cot \mu c\lambda_n) - \lambda_m (\sigma \cot a\lambda_m + \cot \mu c\lambda_m) \} \\ & = 0, \text{ by (46), } m \neq n; \end{aligned}$$

also when $n=m$,

$$\begin{aligned} & \sigma \sin^2 \mu c\lambda_m \int_0^a \sin^2 x\lambda_m dx + \mu \sin^2 a\lambda_m \int_a^b \sin^2 \mu(b-x)\lambda_m dx \\ & = -\frac{\sin^2 a\lambda_m \sin^2 \mu c\lambda_m}{2} \frac{d}{d\lambda} (\sigma \cot a\lambda + \cot \mu c\lambda)_{\lambda=\lambda_m}. \end{aligned}$$

Hence, if we integrate both sides of (49) between the limits 0 and a , and both sides of (50) between the limits a and b , and add the results, we find

$$\begin{aligned} & \int_0^a \sigma F_1(x) \sin \mu c \lambda_m \sin x \lambda_m dx \\ & \quad + \int_a^b \mu F_2(x) \sin a \lambda_m \sin \mu(b-x) \lambda_m dx \\ & = \frac{1}{2} A_m \sin^2 a \lambda_m \sin^2 \mu c \lambda_m \frac{d}{d\lambda} (\sigma \cot a \lambda + \cot \mu c \lambda)_{\lambda=\lambda_m}. \end{aligned}$$

Thus we have the method of determining the coefficients in the proposed series. Taking for $F_1(x)$, $F_2(x)$, respectively the forms

$$1 - \frac{x}{\mu \sigma (b-a) + a} \quad \text{and} \quad \frac{\mu \sigma (b-x)}{\mu \sigma (b-a) + a},$$

relevant to the present enquiry, we find

$$\begin{aligned} A_m &= - \frac{2\sigma \sin \mu c \lambda_m}{\lambda_m \sin^2 a \lambda_m \sin^2 \mu c \lambda_m \frac{d}{d\lambda} (\dots)} \\ &= - \frac{2\sigma}{\lambda} \frac{\operatorname{cosec}^2 a \lambda \operatorname{cosec} \mu c \lambda}{\frac{d}{d\lambda} (\sigma \cot a \lambda + \cot \mu c \lambda)}. \end{aligned}$$

Clearly this is just the form required for our verification. Before leaving this matter it might be of interest to note some verifications of our results for such a theoretical case as that represented by

$$\frac{K_1}{K_2} = \frac{1}{100}, \quad \frac{\kappa_1}{\kappa_2} = \frac{1}{16}, \quad \text{i. e., } \mu = \frac{1}{4}, \quad \sigma = \frac{1}{25}, \quad b-a = 4a.$$

For such a case $f_1(\lambda)$, $f_2(\lambda)$, $f_1'(\lambda)$ as defined above take much simpler forms, and the roots of $f_1(\lambda)=0$ are easily calculated. Considering, *e.g.*, the temperature at $x=a/2$ when $t=0$, we find

$$\begin{aligned} V_1 &= \frac{27}{52} \theta_0 - \frac{4\theta_0}{26\pi} \left(1 + \frac{1}{3} - \frac{1}{5} - \frac{1}{7} + \dots \right) \frac{1}{\sqrt{2}}^* \\ & \quad - \frac{50\theta_0}{26\pi} \left(1 - \frac{1}{3} + \frac{1}{5} - \dots \right) \\ &= 0 \text{ as required;} \end{aligned}$$

* See, *e.g.*, 'Chrystal's Algebra,' pt. ii. p. 335.

or again, taking $b-a=8a$, the other constants being as before, we find that the roots of $f_1(\lambda)=0$ are given by $a\lambda=\beta$, $\pi-\beta$, $\pi+\beta$, $2\pi-\beta$, etc., where $\beta=\tan^{-1}\sqrt{1+2\sigma}$, so that the initial temperature at $x=a$ appears as

$$V_1 = \frac{2}{27}\theta_0 - \frac{2}{27}\theta_0 \sin \beta \left(\frac{1}{\beta} + \frac{1}{\pi-\beta} - \frac{1}{\pi+\beta} - \frac{1}{2\pi-\beta} + \dots \right) \\ = 0 \text{ as required.}$$

§ 7. The present series of problems is concluded by considering the same rod as in the previous case, but where the condition at $x=b$ is that there is radiation into a medium at zero temperature. The solution of this problem does not seem to have been given before. We have at $x=b$, $-K_2 \frac{\partial v_2}{\partial x} = h v_2$, whence $B = \frac{K_2 \mu i \lambda + h}{K_2 \mu i \lambda - h}$. All the other quantities in the integrals (37) and (38) remain as before. With the usual notation, after a somewhat lengthy reduction, we obtain the results

$$v_1 = \frac{\kappa i \theta_0}{\pi} \int_C e^{-\kappa \lambda 2t} \frac{f(\lambda) \cos x\lambda + \phi(\lambda) \sin x\lambda}{f(\lambda)} \lambda d\lambda, \quad \dots \quad (51)$$

$$v_2 = \frac{\kappa i \theta_0}{\pi} \int_C e^{-\kappa \lambda 2t} \frac{2K_1 \{ K_2 \mu \lambda \cos \mu(b-x)\lambda + h \sin \mu(b-x)\lambda \}}{f(\lambda)} \lambda d\lambda, \quad \dots \quad (52)$$

where

$$f(\lambda) = K_2^2 \mu^2 \lambda (\sigma \cos a\lambda \cos \mu c\lambda - \sin a\lambda \sin \mu c\lambda) \\ + K_2 \mu h (\sigma \cos a\lambda \sin \mu c\lambda + \sin a\lambda \cos \mu c\lambda)$$

and

$$\phi(\lambda) = K_2^2 \mu^2 \lambda (\cos a\lambda \sin \mu c\lambda + \sigma \sin a\lambda \cos \mu c\lambda) \\ - K_2 \mu h (\cos a\lambda \cos \mu c\lambda - \sigma \sin a\lambda \sin \mu c\lambda).$$

We evaluate the integrals (51) and (52) in the usual way and subsequently perform the t -integration, thus obtaining

$$V_1 = \theta_0 \left(1 - \frac{K_2 h x}{d} \right) + 2\theta_0 \sum \frac{\phi(\lambda)}{f'(\lambda)} \frac{\sin x\lambda}{\lambda} e^{-\kappa \lambda 2t}, \quad \dots \quad (53)$$

$$V_2 = K_1 \theta_0 \left\{ \frac{K_2 + h(b-x)}{d} \right\} \\ + 2\theta_0 \sum \frac{2K_1 \{ K_2 \mu \lambda \cos \mu(b-x)\lambda + h \sin \mu(b-x)\lambda \} e^{-\kappa \lambda 2t}}{f'(\lambda) \lambda}, \quad \dots \quad (54)$$

where $d = K_1 K_2 + h \{ K_2 a + K_1 (b - a) \}$ and where the summations are with regard to all the positive roots of $f(\lambda) = 0$. The results assume a simpler appearance if we write $\tan \beta$ for $K_2 \mu \lambda / h$ and ψ for $\beta + \mu (b - a) \lambda$. (53) and (54) become respectively

$$V_1 = \theta_0 \left(1 - \frac{K_2 h x}{d} \right) + 2\theta_0 \sum \frac{\sigma \operatorname{cosec}^2 a\lambda}{\frac{d}{d\lambda} (\sigma \cot a\lambda + \cot \psi)} \frac{\sin x\lambda}{\lambda} e^{-\kappa\lambda^2},$$

. . . (55)

$$V_2 = K_1 \theta_0 \left\{ \frac{K_2 - h(b - x)}{d} \right\} + 2\theta_0 \sum \frac{\sigma \operatorname{cosec} a\lambda \operatorname{cosec} \psi}{\frac{d}{d\lambda} (\sigma \cot a\lambda + \cot \psi)} \frac{\sin \{ \beta + \mu(b - x) \}}{\lambda} e^{-\kappa\lambda^2},$$

. . . (56)

the summations now being with regard to all the positive roots of the equation

$$\sigma \cot a\lambda + \cot \psi = 0. \quad (57)$$

The correspondence in form between these last two results and the results (47) and (48) is at once noticed. Further, we may consider the mathematical expansion implied in (55) and (56) as verified in the light of the analysis previously given. The arithmetical aspects of the results obtained in the last two problems might be regarded as of value. Clearly in many ordinary heating processes we have a state of affairs that might be represented approximately by the conditions assumed in these investigations. The layer of low conducting skin often formed on the outside of many heaters acts as a very effective barrier to the free flow of heat through to the metallic parts, and estimates of the heat losses involved would be of great practical interest. The consideration of these and other boundary layer effects is in the meantime deferred*.

In conclusion, I should like to express my thanks to Dr. Green for drawing my attention to his work on the subject of heat conduction and for his very valuable advice given during the preparation of this paper.

* Arithmetical results will be given for the corresponding cylindrical problems at present under investigation.

LXXVI. *The Uniform Positive Column.* By F. LLEWELLYN JONES, D.Phil., M.A. (Lecturer in Physics, University College, Swansea) *.

1. **I**NVESTIGATIONS of discharges through gases in long tubes have shown that a consistent theory of several phenomena is obtained on the hypothesis that positive ions and electrons disappear from the gas by diffusion to the walls of the tube, and that there is no recombination in the gas †. The experiments on both high-frequency and direct-current discharges show that the force in the uniform luminous column is independent of the current, when the heating effect of the current can be neglected. It therefore follows that the numbers of electrons and positive ions per cubic centimetre of the gas are proportional to the current, and it may then be assumed that the supply of electrons and positive ions is maintained by the process of ionization by collision at a rate proportional to the number of electrons per cubic centimetre. Consequently, there must be a positive charge in the gas so that the positive ions and electrons diffuse to the walls at the same rate. At the surface of the tube the electrons recombine with the positive ions, but no appreciable radiation is emitted in the process ‡.

By equating the rate of generation of ions to the rate of loss by diffusion to the walls, the following equation is obtained :—

$$\frac{d^2n}{dr^2} + \frac{1}{r} \frac{dn}{dr} + C^2n = 0, \quad \dots \dots (1)$$

where n is the number of electrons per cubic centimetre in the luminous gas (this is nearly equal to the number of positive ions per cubic centimetre), and §

$$C^2 = \alpha \cdot \frac{\omega_1^2 Z}{K_1 \omega_2}, \quad \dots \dots (2)$$

where α is the coefficient of ionization for the electrons, and K_1 their coefficient of diffusion, Z the uniform longitudinal

* Communicated by Prof. E. J. Evans, D.Sc.

† 'Electricity in Gases,' sect. 302 (Clarendon Press, Oxford, 1915).

‡ J. S. Townsend and M. H. Pakkala, Phil. Mag. xiv. p. 414 (September 1932).

§ J. S. Townsend, Comp. Rend. lxxxvi. p. 55 (January 1928).

potential gradient, ω_1 the mobility of the electrons, and ω_2 that of the positive ions. The solution of equation (1) is

$$n = n_0 J_0(cr),$$

where n_0 is the concentration of the electrons along the axis of the positive column, and n the concentration at a distance r from the axis. If R is the radius of the tube $n_0 J_0(cR)$ is then the concentration at the walls, so that the value of cR depends on the value attributed to the ratio n/n_0 . In the solution of an equation similar to (1) given by Schottky * it is assumed that $n=0$ at the walls of the tube giving $cR=2.4$.

However, from a consideration of the potential difference between the walls and the axis of the tube, it may be seen that the concentration cannot be zero at the surface. This potential difference, V , is equal to

$$\frac{2}{3}E_0 \log\left(\frac{n_0}{n}\right),$$

where E_0 is the mean energy of agitation of the electrons at the axis, so that if $n=0$ at the surface, then $V \rightarrow \infty$. When, following Townsend †, n is taken to be a large fraction of n_0 , about $\frac{1}{2}n_0$, then $cR=1.52$ and $V=.46 E_0$, which is reasonable. Equation (2) can now be written

$$\alpha = \frac{K_1 \omega_2}{\omega_1^2}, \quad \frac{1}{Z} \frac{(1.52)^2}{R^2} \dots \dots \dots (3)$$

Now the experiments on the motions of electrons in gases prove that the ratio Z/p , where Z is the uniform electric force and p the pressure of the gas, is the proper independent variable in terms of which many of the quantities in equation (3) may be expressed. Thus,

$$\frac{\alpha}{p}, \quad pK_1, \quad \omega_1 Z, \quad \text{and} \quad \omega_2 Z,$$

are all functions of the ratio Z/p , so that equation (3) may be re-written ‡

$$\alpha = \frac{B}{R^2 p^2} \left(\frac{Z}{p}\right)^{\frac{1}{2}}, \quad \dots \dots \dots (4)$$

where B is a constant. It follows immediately from this that $R \times p$ is a function of (Z/p) .

* W. Schottky, *Phys. Zeits.* xxv. p. 342 (July 1924).

† J. S. Townsend, *Phil. Mag.* xiii. p. 745 (April 1932).

‡ S. P. MacCallum and F. Llewellyn Jones, *Phil. Mag.* xii. p. 384 (August 1931).

2. It is interesting to investigate the relation between the force and the pressure of the gas in the uniform positive column obtained in this way, and to test the theory by comparing the relation with that found experimentally.

It may be seen from elementary considerations that Z/p must decrease as p increases.

The number of ions produced per second per centimetre of tube is

$$N_1 \alpha_1 \omega_1 Z,$$

where N_1 is the number of electrons in 1 centimetre length of tube. Now α/p and $\omega_1 Z$ are functions of Z/p , therefore the rate of generation of ions is equal to $N_1 \cdot p \cdot \phi(Z/p)$, where $\phi(Z/p)$ increases more rapidly than Z/p , since α/p increases rapidly with Z/p *. For example, in helium α/p is 9×10^{-5} , where Z/p is 1.55 and α/p is $5.3 \cdot 10^{-3}$, when Z/p is 2.43.

The rate at which the ions are thus generated is balanced by the loss due to diffusion to the walls, which is proportional to $K_1 \omega_2 / \omega_1$. As stated above, this quantity is proportional to $1/p \cdot Z/p$. Thus Z/p is proportional to $1/p^2 \cdot \phi(Z/p)$, showing that Z/p must decrease when p increases. This result is quite general, and applicable to all uniform columns of electric discharges through gases at pressures sufficiently high for the diffusion theory to hold; and it is confirmed by the experimental determinations of Z and p . Since

$$\frac{\alpha}{p} = f\left(\frac{Z}{p}\right),$$

equation (4) may be rewritten :

$$\left(\frac{Z}{p}\right)^{-\frac{1}{2}} f\left(\frac{Z}{p}\right) = \frac{B}{R^2 p^2} \cdot \cdot \cdot \cdot \cdot \quad (5)$$

This is the general equation for the uniform positive column which gives the relation between the force Z , the pressure p of the gas, and the radius R of the tube. These results have also been obtained by a different method by Seeliger †, who investigated the particular case when the distribution of the energies of the electrons was Maxwellian, but it is seen from equation (4) that this result is independent of the distribution of the energies.

* J. S. Townsend, *Phil. Mag.* ii. p. 1116 (May 1931).

† R. Seeliger, *Phys. Zeits.* xxxiii. p. 273 (April 1932). [This paper contains a comprehensive account of previous theoretical and experimental investigations on the uniform positive column.]

Unfortunately, there appears to be insufficient experimental evidence to test whether $R \propto p$ is a function of Z/p , at the higher pressures.

In order to find the relation between Z , p , and R , it is necessary to investigate the actual form of the function f .

3. The function f for any gas depends on the nature of the gas, on the process of ionization, on the distribution of the energies of the electrons about the mean energy, and also on the probability of ionization of an atom of the gas in a collision with an electron of a given energy.

Experiments* which have been made in order to determine the form of the ionization function, for the monatomic gases show that the probability of ionization by direct impact with an electron increases from zero to a maximum value, when the energy of the electron is increased above the minimum ionization energy of the atom. For very large energies the probability of ionization decreases. The number of electrons with such high energies is negligible in the positive column of a discharge and need not be considered. Thus the probability of ionization, $P(E_x)$, of an atom in a collision with an electron of energy, E_x , may be represented approximately by the equations:

$$P(E_x) = k \frac{(E_x - V_i)}{E_x}, \quad P(E_x) = 0, \quad \text{when } E_x < V_i, \quad (6)$$

where k is a constant, and V_i is the minimum energy required to ionize an atom.

It is important to consider whether ionization occurs by direct electron impact or through the action of metastable atoms. It is considered by some physicists that metastable atoms of a gas may ionize molecules of other gases and large effects on the conductivity of the monatomic gases may thus be produced by small traces of other gases. In pure gases this cannot occur, but the metastable atoms which are formed may be excited or ionized by collisions of electrons with low energies. The excited atoms radiate and are thus brought back to the normal state. If it be supposed that metastable atoms in pure gases are not brought back to the normal state except by the collisions of electrons, the number of metastable atoms in the gas would be independent of the current. The probability of a metastable atom being destroyed in this

* A. L. L. Hughes and E. Klein, *Phys. Rev.* xxiii. p. 111 (1924); K. T. Compton and C. C. Van Voorhis, *Phys. Rev.* xxvii. p. 724 (1926); P. J. T. Smith, *Phys. Rev.* xxxvi. p. 1293 (1930).

way must be proportional to the number of these electrons, and this may be very great, since a large proportion of the electrons have these low energies. Under these hypotheses the intensity of the radiation emitted from the positive column and the rate of ionization would be proportional to the rate at which metastable atoms are formed; and this is proportional to the current, thus agreeing with experiment.

For the purpose of this investigation, it is interesting to suppose that the probability of the formation of a metastable atom in a collision with an electron of a given energy, E_x , may be presented by equation (6) when V_i is replaced by V_m , the minimum potential required to produce a metastable atom, at least when E_x is not too great. Thus, in these cases the probability of ionization of the atoms of the gas through the action of metastable atoms may still be represented by equation (6).

The distribution of the energies of the electrons is, undoubtedly, affected by processes such as diffusion, which are different from those which set up the Maxwellian distribution. Formulæ representing such distributions have been given by Townsend*, Druyvesteyn†, and Didlauskis‡, in which it is assumed that diffusion is the predominant process in setting up the distribution.

Townsend's formula is approximate and does not take into account all the effects which give rise to inequalities in the energies of the electrons. Both Maxwell's and Townsend's formulæ have been applied in previous researches on the excitation§ and ionization of atoms of helium|| and neon¶ in the positive column. The values of the excitation potentials thus obtained depend on the particular distribution formula assumed. Thus, the results afford a convenient test of the validity of the various formulæ by comparing the calculated potentials with the values deduced from the wave-lengths of the light. In neon, Townsend's formula proves the better; though neither is perfect. In helium, at pressures less than about 15 mm., Maxwell's formula gives results which are in very good agreement with the spectroscopic values.

It is to be noted that this agreement applies only to the

* J. S. Townsend, *Phil. Mag.* ix. p. 1145 (1930).

† J. E. Druyvesteyn, *Physica*, x. p. 61 (1930).

‡ M. Didlauskis, *Zeits. für Phys.* lxxiv. p. 624 (1932).

§ J. S. Townsend and F. Llewellyn Jones, *Phil. Mag.* xii. p. 815 (1931).

|| P. Johnson, *Phil. Mag.* xiii. p. 487 (1932).

¶ J. S. Townsend, *Phil. Mag.* xi. p. 1112 (1931).

distribution of those energies which are much larger than the mean; the electrons with energies more nearly equal to the mean energy may be distributed in an entirely different manner. In these investigations it is not important to know the actual number N_x of electrons with energies greater than E_x , where E_x is large compared with the mean energy E_0 ; but it is necessary to know the ratio N_1/N_2 of the numbers whose energies exceed E_1 and E_2 ; thus, the results show that Maxwell's formula gives this ratio correctly in helium but not in neon.

An investigation into the rate of production of ions in the positive column in mercury vapour has been made by Killian*. At the higher vapour pressures it was found that the loss of ions to the walls by diffusion, which was measured experimentally, may be accounted for by the ionization effected by the direct collisions of electrons with neutral atoms of the gas when the distribution of the energies of the electrons was Maxwellian. The present investigation considers whether a Maxwellian distribution gives the correct values of α/p in discharges at different pressures. These values of α/p have been calculated by Townsend, and it would be easy to test any distribution formula by comparing these values with those obtained from the distribution formula in terms of Z/p or E_0 .

It is thus interesting to consider the function f in the case when the number of electrons within any range of energy is a constant fraction, Y , of the number given by Maxwell's formula, for energies which greatly exceed the mean.

4. Consider the uniform positive column in a cylindrical discharge-tube of radius R . Let the number of electrons in 1 cm. length of tube be N . Then, if the velocities of the electrons with large energies are distributed according to Maxwell's formula, the number of electrons with energies lying between E_x and $E_x + dE$ may be taken to be

$$Y_1 E_0^{-\frac{3}{2}} \cdot E_x^{\frac{1}{2}} \cdot e^{-\frac{3E_x}{2E_0}} \cdot dE,$$

where

$$Y_1 = \sqrt{2} Y \cdot 4\pi \left(\frac{3}{4\pi} \right)^{\frac{3}{2}} \cdot N,$$

and $eE_x = \frac{1}{2}mv^2$, the energy of an electron, and eE_0 is the mean energy of agitation, e being the electronic charge. The number of collisions each electron makes per second with

* T. J. Killian, *Phys. Rev.* xxxv. p. 1238 (1930).

atoms of the gas is vp/L , where L is the mean free path of electrons in the gas at 1 mm. pressure, and p is the pressure of the gas in millimetres. Therefore, the total number of collisions made per second by all these electrons is

$$\sqrt{2} \cdot Y_1 \cdot \frac{p}{L} \cdot \left(\frac{e}{m}\right)^{\frac{1}{2}} \cdot E_0^{-\frac{3}{2}} \cdot E_x \cdot e^{-\frac{3E_x}{2E_0}} \cdot dE_x.$$

If the probability of ionization is given by equation (6), the number of atoms ionized per second by the electrons in this group is

$$\sqrt{2} \cdot Y_1 \cdot \frac{k}{L} \cdot \left(\frac{e}{m}\right)^{\frac{1}{2}} \cdot E_0^{-\frac{3}{2}} \cdot p \cdot (E_x - V) e^{-\frac{3E_x}{2E_0}} \cdot dE_x,$$

where V may be replaced by V_i or V_m , depending on the process of ionization. When $V = V_i$, the expression represents the number of metastable atoms formed which later are ionized in collisions with electrons with small energies. Hence, the total number of atoms ionized per second by all the electrons in 1 cm. of tube, obtained by integrating from $E_x = V$ to $E_x \rightarrow \infty$, is

$$\frac{4\sqrt{2}}{9} \cdot Y_1 \cdot \left(\frac{e}{m}\right)^{\frac{1}{2}} \cdot \frac{k}{L} \cdot p \cdot E_0^{\frac{1}{2}} \cdot e^{-\frac{3V}{2E_0}}.$$

Now this quantity $= \alpha \omega_1 N Z$, where

$$\omega_1 Z = 82 \frac{Z}{p} \cdot \frac{e}{m} \cdot \frac{L}{\bar{v}},$$

$\bar{v}$ being the mean velocity of agitation of the electrons; thus giving

$$\frac{\alpha}{p} = 2 \cdot 2 \frac{kY}{L^2} \cdot \left(\frac{Z}{p}\right)^{-1} \cdot E_0 \cdot e^{-\frac{3V}{2E_0}}.$$

When a stream of electrons moves through a gas in a uniform electric field, the mean energy, E_0 , of the electrons can be expressed as a function of the ratio Z/p when the mean energy is determined by the energy losses in elastic collisions with atoms of the gas. If the mean loss of energy of an electron of energy E_x in an elastic collision with an atom is λE_x , there is a range of values of Z/p within which λ is a constant*, and then the mean energy is given by the equation

$$E_0 = \frac{L}{\sqrt{2\lambda}} \cdot \frac{Z}{p} \cdot \dots \dots \dots (7)$$

* 'Motions of Electrons in Gases' (Clarendon Press, Oxford).

This relation has been verified experimentally for many gases by the lateral diffusion of a stream of electrons moving in a uniform electric field. The equation is true for those values of Z/p which are found in the uniform positive column of discharges through the monatomic gases in wide tubes. Thus, it is reasonable to assume that the mean energy of the electrons in the positive column is proportional to the ratio Z/p .

Hence *,

$$\frac{\alpha}{p} = 2.2 \cdot \frac{kY}{L\sqrt{2\lambda}} \cdot e^{\frac{-3V\sqrt{\lambda}}{\sqrt{2}L}} \cdot \frac{p}{Z}. \quad . \quad . \quad . \quad (8)$$

Substituting this value of α in equation (4), we get

$$C_1 R^2 p^2 = \left(\frac{Z}{v}\right)^{\frac{1}{2}} \cdot e^{\frac{C_2 p}{Z}}, \quad . \quad . \quad . \quad . \quad (9)$$

where

$$C_1 = \frac{2.2 Y k}{B \cdot L \cdot \sqrt{2\lambda}}, \quad \text{and} \quad C_2 = \frac{3V\sqrt{2\lambda}}{2L}.$$

This equation gives the relation between the longitudinal electric force, the pressure of the gas, and the radius of the tube in the uniform positive column, when the distribution of the energies of the electrons with large energies is Maxwellian. The equation is valid for gas pressures sufficiently high for the diffusion theory to be applicable and in wide tubes, so that the mean energy of agitation of the electrons should be proportional to Z/p .

5. In order to test the formula (9), it is interesting to consider helium, because its electrical properties indicate that the fundamental assumptions of the theory (as given in section 3) are approximately fulfilled in discharges through this gas.

The mean energy of agitation of electrons in a gas is determined by the ratio Z/p in uniform electric fields, and by the ratio $\sqrt{2} \cdot A/p$ in oscillating fields, where A is the amplitude of the electric force†. Thus, the formula (9) should apply also to high-frequency discharges, in which case Z is the root mean square of the amplitude of the electric force.

* This expression gives values of α in agreement with those calculated by Townsend for helium.

† J. S. Townsend, *Phil. Mag.* xiii. p. 745 (1932).

In uniform columns of direct-current and high-frequency discharges in helium in wide tubes the ratio Z/p is less than 2 for pressures greater than about 3 mm. In

these cases it has been shown that* $E_0 = 2 \cdot \frac{Z}{p}$, thus from equation (7) it is seen that $\frac{L}{\sqrt{2\lambda}} = 2$, and the constant C_2 in

equation (9) is $3V/4$. The coefficient C_1 cannot be calculated until Yk is known accurately, but it may be found empirically by substituting the measured value of Z for any value of p . The values of the mean force in the uniform positive column of high-frequency discharges in pure helium have been given previously for a tube 3.4 cm. in diameter†. Thus, when $R=1.7$ cm. and $p=4.6$ mm., the r.m.s. value of Z was found to be 9.2 volts per cm., giving $C_1=225$ when $V=24.6$ volts.

The curves representing the change of the force Z with the pressure p , for a tube 3.4 cm. in diameter, is shown in fig. 1, where curve 1 is obtained from equation (9), assuming $V=24.6$ volts, the ionization potential of helium, and curve 2 is given when V is assumed to be 20 volts, the approximate metastable potential. The experimental values of the force are marked by small circles, and for pressures less than 30 mm. the agreement between these values and the theoretical curve 1 of equation (9) may be seen.

6. From this agreement it is possible to calculate the value of Yk , in equation (9), and thus to find the probability of ionization of the helium atom by direct electron impact. It is first necessary to find the constant B of equation (4), from which it may be shown‡ that $B = 7.66 \times 10^{-2}$.

Now $R^2C_1 = 6.6 \times 10^2$, hence, from equation (9), we have that $Yk = 10^{-2}$. The value of k depends on the value assumed for Y . Thus, if the distribution of the energies of the electrons is exactly represented by Maxwell's formula, then $Y=1$, and the maximum probability of ionization is about 1 per cent. This is lower than the value given by the direct experimental determination, which is about 10 per cent.§. This may be accounted for if the fraction Y is

* J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlv. p. 657 (1923).

† J. S. Townsend and F. Llewellyn Jones, *loc. cit.*

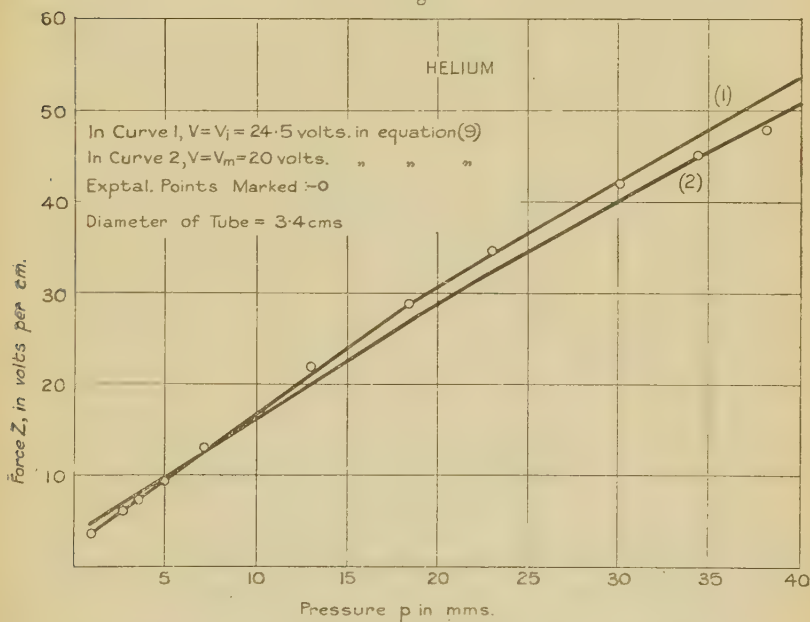
‡ For a similar calculation, see J. S. Townsend, *Phil. Mag.* xi. p. 1116 (1931).

§ P. T. Smith, *loc. cit.*

about 1, indicating that, although the distribution of the energies of the electrons with high energies may be represented by Maxwell's formula, the general distribution is probably not Maxwellian, because the actual numbers of those electrons with the higher energies is only about one-tenth of the numbers given by Maxwell's formula.

It may be noticed that, when ionization is assumed to be due entirely to the action of metastable atoms, the agreement between the formula (9) [curve 2, fig. 1] and the

Fig. 1.

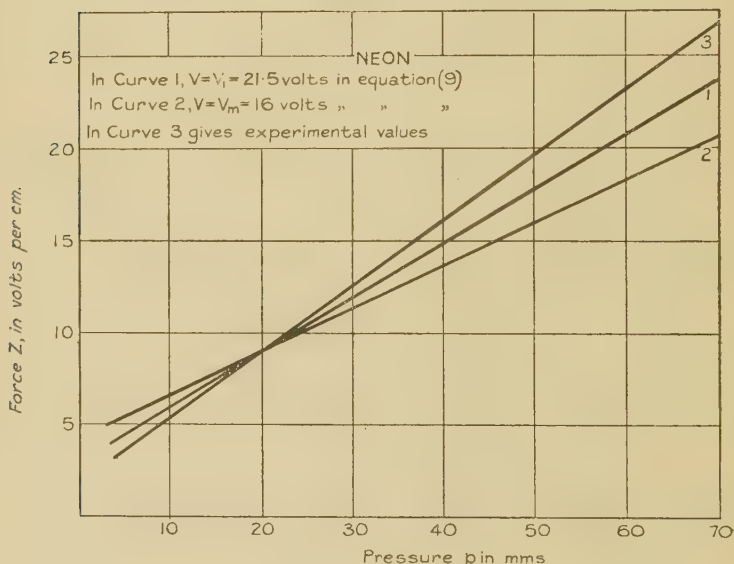


experimental value is not so good, for pressures less than 30 mm., as in the case of single electron impact [curve 1, fig. 1]. However, for higher pressures, the experimental determinations tend to agree more with curve 2, thus indicating that metastable atoms may here be taking an important part in the process of ionization. At these pressures also the band spectrum of helium is very prominent in comparison with the line spectrum.

The curves obtained when equation (9) is applied to neon are given in fig. 2, where for curve 1, V was assumed to be

21.5 volts, the ionization potential, and for curve 2, V was assumed to be 16.5 volts, the metastable potential. Both curves deviate from curve 3, which gives the experimental values*, thus confirming the conclusions of section 3, where it was considered that the distribution of the energies of the electrons in neon may not be represented by Maxwell's formula.

Fig. 2.



I am indebted to Professor J. S. Townsend for much helpful criticism.

Added in proof.—Since the above was written I find that Druyvesteyn (*Phys. Zeits.* xxxiii. p. 856 (1932)) has derived a distribution formula suitable for low pressures, and has calculated α/p in the neon positive column. He finds good agreement with the experimental values of Townsend and MacCallum.

January 1933.

* P. Johnson, *Phil. Mag.* x. p. 921 (Nov. 1930).

LXXVII. *The Equilibrium of a Tooth with a General Conical Root.* By J. L. SYNGE, Sc.D., Professor of Applied Mathematics, University of Toronto*.

SYNOPSIS.

Part I.—INTRODUCTORY.

1. Introduction.
2. The General Theory.

Part II.—GENERAL METHOD FOR A CONICAL ROOT.

3. Two Coordinate Systems on a Cone.
4. The Normal Displacement and the Geometrical Constants.
5. The Pressure Distribution over a Conical Root.
6. The Applied Force System and the Displacement of the Tooth.

Part III.—THE CASE OF A ROOT WITH AN EQUILATERAL TRIANGULAR SECTION.

7. Calculation of the Geometrical Constants.
8. Relations between the Applied Force System and the Displacement.
9. The Pressure Distribution.
10. Some Numerical Results.

Part I.—INTRODUCTORY.

1. *Introduction.*

IN a paper written recently and not yet published † I have investigated the equilibrium of a tooth (human or animal) on the assumption that the thin periodontal membrane, which lies between the root of the tooth and the bone, may be treated as an isotropic elastic solid, incompressible but of finite rigidity. The partial differential equation of the problem is the same as that employed by Reynolds ‡ in his classical theory of a thin layer of lubricant. In the paper referred to I have applied the theory to the two-dimensional case and also to the case where the root of the tooth is a solid of revolution: in particular, I have treated the case where the root is a right circular cone. Expressions are obtained for the displacement of the tooth and the distribution of pressure in the membrane when

* Communicated by the Author. Read at the International Congress of Mathematicians, Zürich, 1932.

† To appear in *Phil. Trans. Roy. Soc. A.*

‡ O. Reynolds, "On the Theory of Lubrication," *Phil. Trans. Roy. Soc. pt. i.* 1886; 'Papers on Mechanical and Physical Subjects,' ii. pp. 228–311.

assigned forces are applied to the crown of the tooth under the assumption that the membrane is of constant thickness.

But while the case of a root of revolution leads to comparatively simple mathematical results, such a form of root is hardly likely to occur in nature: it suffers from the serious defect that if there is applied to such a tooth a force having a moment about the axis of symmetry of the root the periodontal membrane will undergo a finite strain. In nature the usual form of cross-section is oval or triangular with rounded corners. It is, of course, understood that the tooth in question has a single root.

In dealing mathematically with a problem in physiology it is not possible (except for statements of the most general character) to attempt a close agreement between the geometrical forms assumed in the mathematical theory and the actual geometrical forms of nature. We are compelled to select simple models, approximating roughly to the natural forms. Thus, in the paper referred to the model of the root was of revolution. In the present paper the model of the root is a *cone*, which, definitely, is not right-circular. After briefly reviewing the results of the general theory we shall assume that the membrane is of constant thickness, and proceed with general developments applicable to the case of a conical root. We shall determine the distribution of pressure in the membrane, corresponding to an assigned displacement of the tooth, and we shall give linear equations expressing the six components of the force system applied to the tooth in terms of the six components of the infinitesimal displacement of the tooth. The above expressions involve certain geometrical constants whose values depend solely on the geometrical form of the conical root. Their evaluation requires only the use of quadratures. It should be pointed out that the theory (for the sake of mathematical simplicity) deviates from nature in two respects: (i.) the membrane is assumed to be of uniform thickness, (ii.) the edge of the membrane is assumed to be at a constant distance from the apex of the conical root, the measurement being made along the generators of the cone.

In Part III. I discuss the case where the root is assumed to have a cross-section of the form of an equilateral triangle. The geometrical constants are explicitly evaluated and other detailed results obtained.

2. *The General Theory.*

We shall here state the results of the general theory which we shall apply to the case of the conical root.

The tooth is regarded as a rigid body, separated from the bone or socket by an incompressible membrane of small thickness h (in general varying over the surface of the root); the membrane is attached both to the root and to the bone, having a free edge subject to atmospheric pressure P . If x^j ($j=0, 1, 2$) denote any system of curvilinear co-ordinates and u^j ($j=0, 1, 2$) denote the components of displacement ($u^j=dx^j$) in the membrane, the covariant strain-tensor is

$$e_{jk} = \frac{1}{2}(A_j u_k + A_k u_j), \quad . \quad . \quad . \quad . \quad (2.1)$$

where A_j is a symbol of covariant derivation with respect to the spatial line-element

$$ds^2 = a_{jk} dx^j dx^k, \quad . \quad . \quad . \quad . \quad (2.2)$$

where repeated Latin suffixes are summed over the range 0, 1, 2. If T_{jk} denote the components of the covariant stress-tensor, the stress-strain relations for an incompressible elastic body are

$$T_{jk} = -p a_{jk} + 2\mu e_{jk}, \quad . \quad . \quad . \quad . \quad (2.3)$$

where p is a "hydrostatic" pressure and μ is the rigidity. The equations of equilibrium are (in the absence of body forces, gravity being neglected)

$$A_k T_j^k = 0, \quad . \quad . \quad . \quad . \quad (2.4)$$

which give, on substitution from (2.3),

$$A^j p = \mu A^k A_k u^j, \quad . \quad . \quad . \quad . \quad (2.5)$$

suffixes being lowered or raised in the usual way by means of the tensors a_{jk} , a^{jk} . In addition to (2.5) we have, as the fourth equation for the four unknowns u^j , p , the equation of incompressibility

$$A_j u^j = 0. \quad . \quad . \quad . \quad . \quad (2.6)$$

Taking a coordinate system in which x^0 is the normal distance from the bone and x^α ($\alpha=1, 2$) are any curvilinear coordinates on the bone (or on the root of the tooth), we seek solutions of our equations (2.5), (2.6) in the form of power series in a parameter which is made to tend to zero with the thickness h of the membrane. Thus we find for the principal parts of the quantities u^j , p the following results:

$$u^\alpha = \frac{1}{2\mu} x^0 (x^0 - h) B^\alpha p, \quad . \quad . \quad . \quad . \quad (2.7)$$

$$u^0 = -\frac{1}{2\mu} \left\{ \frac{1}{3} (x^0)^3 - \frac{1}{2} h (x^0)^2 \right\} B^\alpha B_\alpha p + \frac{1}{4\mu} h^2 (B^\alpha h) (B_\alpha p), \quad (2.8)$$

while p satisfies the partial differential equation

$$B^a(h^3 B_a p) = 12\mu\beta, \quad . \quad . \quad . \quad (2.9)$$

subject to the boundary conditions $p=P$ at the edge of the membrane; in these expressions h (in general a function of x^1, x^2) is the thickness of the membrane, β is the normal component (at any point x^1, x^2 of the root) of the displacement of the root (caused by the application of external forces to the crown of the tooth and counted positive when in the sense from bone to root), and B_a, B^a are symbols of covariant and contravariant derivation with respect to the metric of the surface of the root,

$$ds^2 = b_{\alpha\beta} dx^\alpha dx^\beta. \quad . \quad . \quad . \quad (2.10)$$

We use Greek suffixes to denote a range or summation over the values 1, 2.

A more convenient, if less compact, form of (2.9) is

$$b^{-\frac{1}{2}} \frac{\partial}{\partial x^\alpha} \left(b^{\frac{1}{2}} h^3 b^{a\beta} \frac{\partial p}{\partial x^\beta} \right) = 12\mu\beta, \quad . \quad . \quad (2.11)$$

where b is the determinant $|b_{\alpha\beta}|$.

The displacement of the root as a result of the application of finite forces to the crown is of the order of h^3 . It is evident that the strain is a small strain, a fact which justifies us in the application of the ordinary equations of elasticity.

The principal part of the stress is the pressure p .

The general problem is as follows: to the crown of a tooth whose root is of known shape, with membrane of known thickness and rigidity, there are applied (in addition to an atmospheric pressure P) given finite external forces. We wish to know (i.) the displacement which the tooth undergoes as a result of the application of these forces, (ii.) the distribution of pressure throughout the membrane.

It is easy to write down the six equations of statical equilibrium of the tooth connecting the external forces with the pressure distribution over the root; if y_j ($j=1, 2, 3$) is any system of rectangular Cartesian coordinates, for which the external forces reduce to a force F_j at the origin and a couple G (Latin subscripts having now and henceforth the range or summation 1, 2, 3), and if λ_j are the direction cosines of the normal to the root, in the sense from bone to root, then the equations of equilibrium are

$$\left. \begin{aligned} F_j + \iint \lambda_j (p - P) dS &= 0, \\ G_j + \iiint (y \times \lambda)_j (p - P) dS &= 0, \end{aligned} \right\} \quad . \quad . \quad (2.12)$$

where the integrals are taken over that part of the surface of the root covered by the membrane, and $(y \times \lambda)_j$ is the j th component of the vector product.

The displacement of the tooth may be reduced to an infinitesimal translation with components v_j along the axes of y_j and an infinitesimal rotation with components ω_j about an axis through the origin. Then the normal displacement of the root is

$$\beta = \lambda_j v_j + \lambda_j (\omega \times y)_j = \lambda_j v_j + \omega_j (y \times \lambda)_j. \quad (2.13)$$

Now x^1, x^2 being, as above, any curvilinear coordinates on the surface of the root, the equations of the root may be expressed in the form

$$y_j = y_j(x^1, x^2); \quad . \quad . \quad . \quad . \quad (2.14)$$

λ_j are then known as functions of x^1, x^2 . Thus the β of (2.13) is a known function of x^1, x^2 and of the components of displacement. Substituting it in (2.9) we have a partial differential equation for p ; solving this, with the assigned boundary condition $p=P$ at the edge of the membrane, we have p as a function of $x^1, x^2, v_1, v_2, v_3, \omega_1, \omega_2, \omega_3$. Substituting in (2.12), we have six equations connecting the six components of external force, F_j, G_j , and the six components of displacement v_j, ω_j . Solving these equations, we may find the displacement corresponding to given external forces and at the same time the principal part of the stress in the membrane, namely, p . If we are interested in the displacement in the membrane, we can find it by (2.7), (2.8).

Part. II.—GENERAL METHOD FOR A CONICAL ROOT.

3. Two Coordinate Systems on a Cone.

The most essential step in the investigation of the equilibrium of a tooth is the integration of the partial differential equation (2.9) or (2.11). We shall assume the thickness of the membrane (h) to be constant over the root: thus our equation may be written

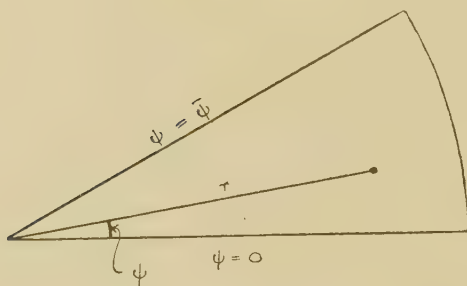
$$\Delta p = 12\mu\beta/h^3, \quad . \quad . \quad . \quad . \quad (3.1)$$

where Δ is the two-dimensional Laplacian operator ($B^a B_a$) on the curved surface of the root and β is the normal component of the displacement of the root, counted positive when away from the bone. The Gaussian coordinates on the surface of the root are quite arbitrary.

In order to integrate the equation we wish to reduce it to the simplest possible form by suitable choice of Gaussian coordinates. Since the surface of the conical root is developable, its intrinsic geometry is that of a plane, and to obtain a simple form for Δp we should employ as Gaussian coordinates a pair which develop (when the surface of the cone is developed into a plane) into rectangular Cartesian coordinates or a closely related system. The best system appears to be that of polar coordinates r, ψ in the plane development of the cone, such that the apex O of the root is $r=0$ and the edges of the wedge-like development are $\psi=0$ and $\psi=\bar{\psi}$ (fig. 1). With these coordinates we have

$$\Delta p = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial p}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 p}{\partial \psi^2}. \quad \dots \quad (3.2)$$

Fig. 1.



But while the system (r, ψ) makes Δp assume a simple form, it is not easy to express the normal displacement β in terms of these coordinates. We find it convenient to introduce another system of surface coordinates (z, u) as follows. If (y_1, y_2, y_3) is any system of rectangular Cartesian coordinates, having the apex O for origin, the shape of the cone may be described by means of its section by the plane $y_3=1$. Let the parametric equations of this section be

$$y_1 = f_1(u), \quad y_2 = f_2(u), \quad \dots \quad (3.3)$$

where u is a parameter ranging from 0 to 2π as we pass round the section in the sense which takes us from the axis of y_1 to that of y_2 . We shall suppose the axes chosen so that the axis of y_3 lies inside the cone, and we shall make $u=0$ correspond to $y_2=0, y_1>0$. The equations of the cone are then (in parametric form)

$$y_1 = z f_1(u), \quad y_2 = z f_2(u), \quad y_3 = z. \quad \dots \quad (3.4)$$

We have now to connect z, u with the coordinates r, ψ . Let $\psi=0$ correspond to $u=0$, and therefore $\psi=\bar{\psi}$ to $u=2\pi$. Since the lines $\psi=\text{const.}$ are the same as the lines $u=\text{const.}$ (being generators of the cone), the transformation is of the form

$$r = r(z, u), \quad \psi = \psi(u). \quad (3.5)$$

We have

$$r = z(1 + f_1^2 + f_2^2)^{\frac{1}{2}}, \quad (3.6)$$

and proceeding along the section of the root by $z=\text{const.}$ we have, denoting derivatives by accents,

$$\left(r \frac{d\psi}{du} du\right)^2 = (dy_1^2 + dy_2^2) \frac{f_1'^2 + f_2'^2 + (f_1 f_2' - f_2 f_1')^2}{(1 + f_1^2 + f_2^2)(f_1'^2 + f_2'^2)}, \quad (3.7)$$

so that

$$\psi = \int_0^u \gamma(1 + f_1^2 + f_2^2)^{-1} du, \quad (3.8)$$

where γ is given by

$$\gamma^2 = f_1'^2 + f_2'^2 + (f_1 f_2' - f_2 f_1')^2, \quad \gamma > 0. \quad (3.9)$$

Then $\bar{\psi}$ is given by

$$\bar{\psi} = \int_0^{2\pi} \gamma(1 + f_1^2 + f_2^2)^{-1} du. \quad (3.10)$$

If we take for u the polar angle (measured from the axis of y_1 , as in fig. 2) in the plane $y_3=1$, we may write the equation of the section of the root by that plane in the form

$$(y_1^2 + y_2^2)^{\frac{1}{2}} = (f_1^2 + f_2^2)^{\frac{1}{2}} \equiv \Phi(u). \quad (3.11)$$

Then

$$f_1 = \Phi \cos u, \quad f_2 = \Phi \sin u, \quad (3.12)$$

and

$$\left. \begin{aligned} f_1' &= \Phi' \cos u - \Phi \sin u, & f_2' &= \Phi' \sin u + \Phi \cos u, \\ f_1^2 + f_2^2 &= \Phi^2 = f_1 f_2' - f_2 f_1', & f_1 f_1' + f_2 f_2' &= \Phi \Phi', \\ f_1'^2 + f_2'^2 &= \Phi^2 + \Phi'^2, & \gamma &= (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}. \end{aligned} \right\} \quad (3.13)$$

Thus from (3.8) we have for the connexion between ψ and u

$$\psi = \int_0^u (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}} (1 + \Phi^2)^{-1} du, \quad (3.14)$$

and from (3.10)

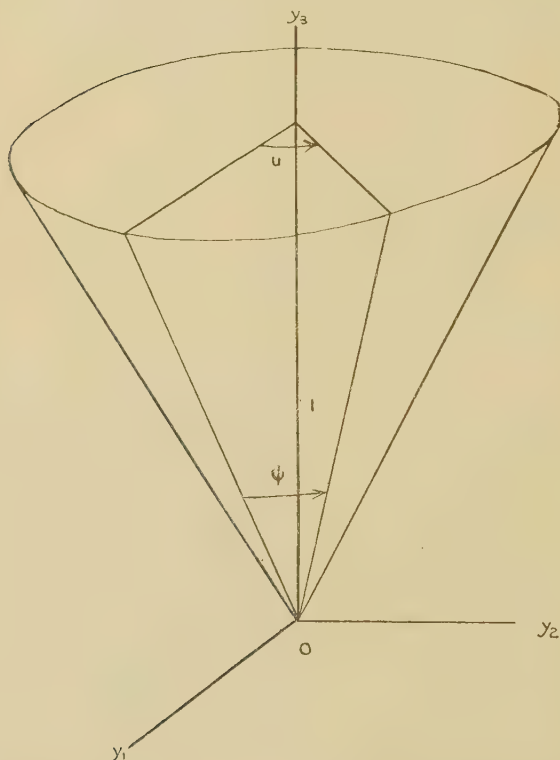
$$\bar{\psi} = \int_0^{2\pi} (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}} (1 + \Phi^2)^{-1} du. \quad (3.15)$$

4. *The Normal Displacement and the Geometrical Constants.*

We have now to evaluate the normal displacement β corresponding to a general infinitesimal displacement v_j , ω_j of the tooth. The direction cosines of the normal to the root are proportional to

$$\frac{\partial(y_2, y_3)}{\partial(z, u)}, \quad \frac{\partial(y_3, y_1)}{\partial(z, u)}, \quad \frac{\partial(y_1, y_2)}{\partial(z, u)},$$

Fig. 2



and hence by (3.4) we have for these direction cosines (in the sense from bone to root)

$$\left. \begin{aligned} \lambda_1 &= -\gamma^{-1}f_2', & \lambda_2 &= \gamma^{-1}f_1', & \lambda_3 &= \gamma^{-1}(f_1f_2' - f_2f_1'), \\ \lambda_1 + i\lambda_2 &= i\gamma^{-1}(f_1' + if_2'), \end{aligned} \right\} \quad (4.1)$$

where γ is given by (3.9) and $i = \sqrt{-1}$.

The normal displacement β (positive in the sense from bone to tooth) is given by (2.13). Let η_j be the direction cosines of a generator of the cone, so that

$$y_j = r\eta_j, \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

and therefore

$$\left. \begin{aligned} \eta_1 &= f_1(1 + f_1^2 + f_2^2)^{-\frac{1}{2}}, & \eta_2 &= f_2(1 + f_1^2 + f_2^2)^{-\frac{1}{2}}, \\ \eta_3 &= (1 + f_1^2 + f_2^2)^{-\frac{1}{2}}, \end{aligned} \right\} \quad (4.3)$$

and

$$\left. \begin{aligned} (\eta \times \lambda)_1 &= \eta_2 \lambda_3 - \eta_3 \lambda_2 \\ &= \gamma^{-1}(1 + f_1^2 + f_2^2)^{-\frac{1}{2}} \{f_2(f_1 f_2' - f_2 f_1') - f_1'\}, \\ (\eta \times \lambda)_2 &= \eta_3 \lambda_1 - \eta_1 \lambda_3 \\ &= -\gamma^{-1}(1 + f_1^2 + f_2^2)^{-\frac{1}{2}} \{f_1(f_1 f_2' - f_2 f_1') + f_2'\}, \\ (\eta \times \lambda)_3 &= \eta_1 \lambda_2 - \eta_2 \lambda_1 \\ &= \gamma^{-1}(1 + f_1^2 + f_2^2)^{-\frac{1}{2}} (f_1 f_1' + f_2 f_2'). \end{aligned} \right\} \quad (4.4)$$

In terms of the function Φ introduced in (3.11) we have therefore

$$\left. \begin{aligned} \lambda_1 + i\lambda_2 &= \frac{e^{iu}(i\Phi' - \Phi)}{(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}}, \\ \lambda_3 &= \frac{\Phi^2}{(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}}, \\ (\eta \times \lambda)_1 + i(\eta \times \lambda)_2 &= \frac{e^{iu}(-\Phi' - i\Phi - i\Phi^3)}{(1 + \Phi^2)^{\frac{1}{2}}(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}}, \\ (\eta \times \lambda)_3 &= \frac{\Phi\Phi'}{(1 + \Phi^2)^{\frac{1}{2}}(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}}. \end{aligned} \right\} \quad (4.5)$$

Since λ_j , $(\eta \times \lambda)_j$ are periodic in ψ , with period $\bar{\psi}$, we may expand in Fourier series:

$$\left. \begin{aligned} \lambda_j &= \sum_{n=-\infty}^{\infty} A_j^{(n)} e^{2n\pi i \psi / \bar{\psi}}, \\ (\eta \times \lambda)_j &= \sum_{n=-\infty}^{\infty} B_j^{(n)} e^{2n\pi i \psi / \bar{\psi}}, \end{aligned} \right\} \quad . \quad . \quad . \quad (4.6)$$

where the A's and B's are complex constants, $A_j^{(-n)}$ being conjugate to $A_j^{(n)}$ and $B_j^{(-n)}$ conjugate to $B_j^{(n)}$, and

$$\left. \begin{aligned} A_j^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} \lambda_j e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ B_j^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} (\eta \times \lambda)_j e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ (n &= \dots -2, -1, 0, 1, 2, \dots). \end{aligned} \right\} \quad \cdot \cdot \quad (4.7)$$

These quantities depend only on the geometrical shape of the conical root: we may refer to them as its *geometrical constants*. They may also be expressed as follows:—

$$\left. \begin{aligned} A_1^{(n)} &= -\bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\Phi' \sin u + \Phi \cos u}{(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ A_2^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\Phi' \cos u - \Phi \sin u}{(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ A_1^{(n)} \pm i A_2^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\pm i \Phi' - \Phi}{(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{\pm i u - 2n\pi i \psi / \bar{\psi}} d\psi, \\ A_3^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\Phi^2}{(\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ B_1^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\psi - \Phi' \cos u + (\Phi + \Phi^3) \sin u}{(1 + \Phi^2)^{\frac{1}{2}} (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ B_2^{(n)} &= -\bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\psi \Phi' \sin u + (\Phi + \Phi^3) \cos u}{(1 + \Phi^2)^{\frac{1}{2}} (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ B_1^{(n)} \pm i B_2^{(n)} &= \pm i \bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\pm i \Phi' - \Phi - \Phi^3}{(1 + \Phi^2)^{\frac{1}{2}} (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{\pm i u - 2n\pi i \psi / \bar{\psi}} d\psi, \\ B_3^{(n)} &= \bar{\psi}^{-1} \int_0^{\bar{\psi}} \frac{\Phi \Phi'}{(1 + \Phi^2)^{\frac{1}{2}} (\Phi^2 + \Phi'^2 + \Phi^4)^{\frac{1}{2}}} e^{-2n\pi i \psi / \bar{\psi}} d\psi, \\ (n &= \dots -2, -1, 0, 1, 2, \dots). \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (4.8)$$

By (2.13) and (4.6) the normal displacement is

$$\beta = \lambda_j v_j + r \omega_j (\eta \times \lambda)_j = \sum_{n=-\infty}^{\infty} (A_j^{(n)} v_j + r B_j^{(n)} \omega_j) e^{2n\pi i \psi / \bar{\psi}}, \quad (4.9)$$

where the convention of summation over the range 1, 2, 3 with respect to repeated Latin subscripts to be remembered.

5. The Pressure Distribution over a Conical Root.

We have now to solve the partial differential equation (3.1) or

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial p}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 p}{\partial \psi^2} = \nu \sum_{n=-\infty}^{\infty} A_j^{(n)} v_j e^{2n\pi i \psi / \sqrt{\psi}} + r\nu \sum_{n=-\infty}^{\infty} B_j^{(n)} \omega_j e^{2n\pi i \psi / \sqrt{\psi}}, \quad (5.1)$$

where we have written for brevity

$$\nu = 12\mu/h^3. \quad . \quad . \quad . \quad . \quad . \quad (5.2)$$

The boundary conditions will be as follows:—(i.) p is to be single-valued for $r=0$, (ii.) $p=P$ (the atmospheric pressure) at the edge of the membrane. We shall investigate the simplest form of edge: *we shall assume that every point at the edge of the membrane is equidistant from the apex O*, so that the equation of the free edge is

$$r = c, \quad . \quad . \quad . \quad . \quad . \quad (5.3)$$

where c is a constant. If we adopt tentatively a solution of the form

$$p = \sum_{n=-\infty}^{\infty} p^{(n)} e^{2n\pi i \psi / \sqrt{\psi}}, \quad . \quad . \quad . \quad . \quad (5.4)$$

where $p^{(n)}$ are complex functions of r , $p^{(-n)}$ being conjugate to $p^{(n)}$, the boundary conditions are

$$\left. \begin{array}{l} \text{for } r=0: \quad p^{(n)} = p^{(-n)} = 0, \quad (n=1, 2, \dots); \\ \text{for } r=c: \quad p^{(0)} = P, \quad p^{(n)} = p^{(-n)} = 0, \quad (n=1, 2, \dots). \end{array} \right\} \quad (5.5)$$

Substituting from (5.4) in (5.1), we have to satisfy

$$\left. \begin{array}{l} \frac{1}{r} \frac{d}{dr} \left(r \frac{dp^{(n)}}{dr} \right) - \left(\frac{2n\pi}{\sqrt{\psi}} \right)^2 \frac{p^{(n)}}{r^2} = \nu A_j^{(n)} v_j + r\nu B_j^{(n)} \omega_j, \\ (n=\dots-2, -1, 0, 1, 2, \dots). \end{array} \right\} \quad (5.6)$$

The integration of these equations is immediate; we find, using the boundary conditions (5.5) and the condition that $p^{(0)}$ be finite for $r=0$,

$$p^{(0)} = P + \frac{\nu}{4} A_j^{(0)} v_j (r^2 - c^2) + \frac{\nu}{9} B_j^{(0)} \omega_j (r^3 - c^3), \quad . \quad . \quad . \quad (5.7)$$

$$p^{(n)} = \frac{\nu c^2 A_j^{(n)} v_j}{4 - (2n\pi/\bar{\psi})^2} \left\{ \left(\frac{r}{c} \right)^2 - \left(\frac{r}{c} \right)^{2|n|\pi/\bar{\psi}} \right\} + \frac{\nu c^3 B_j^{(n)} \omega_j}{9 - (2n\pi/\bar{\psi})^2} \left\{ \left(\frac{r}{c} \right)^3 - \left(\frac{r}{c} \right)^{2|n|\pi/\bar{\psi}} \right\}, \quad (5.8)$$

($n = \dots -2, -1, 1, 2, \dots$).

Hence we may state this result: *when a tooth with a conical root, having the equations (3.4), receives an infinitesimal displacement consisting of a translation v_j and a rotation ω_j about an axis through the apex O, then the pressure in the membrane (assumed of uniform thickness h) is given by*

$$p = P + \nu c^2 \sum_{n=-\infty}^{\infty} \frac{(r/c)^2 - (r/c)^{2|n|\pi/\bar{\psi}}}{4 - (2n\pi/\bar{\psi})^2} A_j^{(n)} v_j e^{2n\pi i \psi/\bar{\psi}} + \nu c^3 \sum_{n=-\infty}^{\infty} \frac{(r/c)^3 - (r/c)^{2|n|\pi/\bar{\psi}}}{9 - (2n\pi/\bar{\psi})^2} B_j^{(n)} \omega_j e^{2n\pi i \psi/\bar{\psi}}, \quad (5.9)$$

where P is the atmospheric pressure, $\nu = 12\mu/h^3$ (μ being the rigidity of the membrane), c is the distance from the apex to the edge of the membrane (assumed constant), r, ψ are polar coordinates in the plane development of the surface of the root, $\bar{\psi}$ is the increment in ψ on passing round the root, and the A 's and B 's are certain constants, given by (4.7) or (4.8), depending only on the shape of the conical root. Where the subscript j is repeated in the above expressions a summation over the range 1, 2, 3 is understood.

The pressure at the apex is

$$p = (p^{(0)})_{r=0} = P - \frac{\nu c^2}{4} A_j^{(0)} v_j - \frac{\nu c^3}{9} B_j^{(0)} \omega_j. \quad (5.10)$$

6. The Applied Force System and the Displacement of the Tooth.

To find the connexion between the applied force system F_j, G_j and the displacement of the tooth v_j, ω_j , we refer to (2.12), in which we are to substitute the series (4.6) for λ_j and $(\eta \times \lambda)_j$ and the series given in (5.9) for $p - P$. We have

$$dS = r dr d\psi, \quad \dots \dots \dots (6.1)$$

and thus

$$\left. \begin{aligned} F &= - \int_{r=0}^c \int_{\psi=0}^{\bar{\psi}} \lambda_j (p-P) r \, dr \, d\psi \\ &= \nu \bar{\psi} \sum_{n=-\infty}^{\infty} A_j^{(n)} \left\{ \frac{c^4 A_k^{(-n)} v_k}{4(2+2|n|\pi/\bar{\psi})^2} \right. \\ &\quad \left. + \frac{c^5 B_k^{(-n)} \omega_k}{5(2+2|n|\pi/\bar{\psi})(3+2|n|\pi/\bar{\psi})} \right\}, \\ G_j &= - \int_{r=0}^c \int_{\psi=0}^{\bar{\psi}} (\eta \times \lambda)_j (p-P) r^2 \, dr \, d\psi \\ &= \nu \bar{\psi} \sum_{n=-\infty}^{\infty} B_j^{(n)} \left\{ \frac{c^5 A_k^{(-n)} v_k}{5(2+2|n|\pi/\bar{\psi})(3+2|n|\pi/\bar{\psi})} \right. \\ &\quad \left. + \frac{c^6 B_k^{(-n)} \omega_k}{6(3+2|n|\pi/\bar{\psi})^2} \right\}. \end{aligned} \right\} \quad (6.2)$$

These express the force system applied to the tooth in terms of the resultant displacement: here, as before, $\nu = 12\mu/h^3$, $\bar{\psi}$ is the increment in ψ in passing round the root, c the slant-length of the membrane (assumed constant) and the A 's and B 's the complex geometrical constants given by (4.7) or (4.8). The solution of the problem of the equilibrium of a tooth of the general conical type considered reduces therefore to the calculation of these geometrical constants.

If we wish to know the pressure distribution corresponding to a given applied force system, we are to solve (6.2) for the components of displacement in terms of the force system and substitute in (5.9). It is clear that the constant ν will disappear, and thus *the pressure distribution corresponding to a given force system is independent of the values of the rigidity of the membrane and of its thickness* (provided, of course, that the latter is very small, as is assumed throughout).

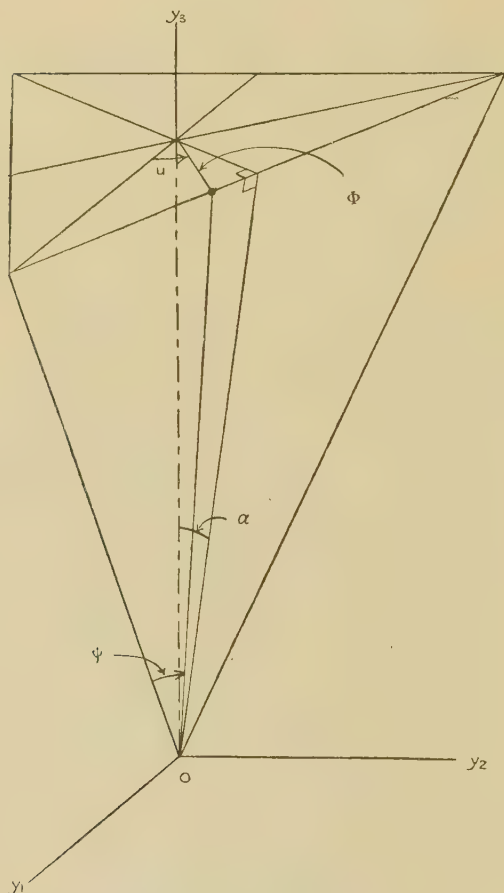
Part III.—THE CASE OF A ROOT WITH AN EQUILATERAL TRIANGULAR SECTION.

7. Calculation of the Geometrical Constants.

The root of the upper central tooth is frequently found to have a cross-section which may be regarded as a triangle with rounded corners. As an idealization of this we shall suppose that the section is an equilateral triangle. Let the

axis of y_3 cut this section normally at its centroid, and let the axis of y_1 be perpendicular to one of the sides of the triangle (fig. 3). Let α be the inclination to the axis of y_3 of any one of the flat faces of the root. Taking u to be the

Fig. 3.



inclination to the axis of y_1 of a radius vector in the section, we have for the function Φ of (3.11), which gives the polar equation of the cross-section by $y_3=1$,

$$\Phi(u) = \tan \alpha \sec(u - q\pi), \quad 0 < u < 2\pi, \quad (7.1)$$

where

$$\left. \begin{aligned} q &= 1/3 & \text{for } 0 < u < 2\pi/3, \\ q &= 1 & \text{for } 2\pi/3 < u < 4\pi/3, \\ q &= 5/3 & \text{for } 4\pi/3 < u < 2\pi. \end{aligned} \right\} \quad . \quad . \quad (7.2)$$

Then

$$\left. \begin{aligned} \Phi^2 + \Phi'^2 &= \tan^2 \alpha \sec^4 (u - q\pi), \\ \Phi^2 + \Phi'^2 + \Phi^4 &= \tan^2 \alpha \sec^2 \alpha \sec^4 (u - q\pi), \\ \pm i\Phi' - \Phi &= -\tan \alpha \sec^2 (u - q\pi) e^{\mp i(u - q\pi)}, \end{aligned} \right\} \quad (7.3)$$

and, by (3.14),

$$\psi = \int_0^u \frac{\tan \alpha \sec \alpha \sec^2 (u - q\pi)}{1 + \tan^2 \alpha \sec^2 (u - q\pi)} du. \quad . \quad . \quad (7.4)$$

The total increment in ψ in passing round the root is easily seen from geometrical considerations to be

$$\bar{\psi} = 6 \tan^{-1} (\sqrt{3} \cdot \sin \alpha), \quad . \quad . \quad . \quad (7.5)$$

so that

$$\sin \alpha = (1/\sqrt{3}) \tan (\bar{\psi}/6). \quad . \quad . \quad . \quad (7.6)$$

From (7.4), or more directly from the figure,

$$\psi = \frac{1}{2} q \bar{\psi} + \tan^{-1} (\sin \alpha \tan (u - q\pi)), \quad . \quad . \quad (7.7)$$

where " $\tan^{-1}$ " denotes an angle between $-\frac{1}{2}\pi$ and $\frac{1}{2}\pi$: we have

$$\sin \alpha \tan (u - q\pi) = \tan (\psi - \frac{1}{2} q \bar{\psi}). \quad . \quad . \quad (7.8)$$

Let us now evaluate the geometrical constants from (4.8). We have

$$\left. \begin{aligned} A_1^{(n)} \pm i A_2^{(n)} &= -\bar{\psi}^{-1} \cos \alpha \int_0^{\bar{\psi}} e^{\pm q\pi i - 2n\pi i \psi / \bar{\psi}} d\psi, \\ A_3^{(n)} &= \bar{\psi}^{-1} \sin \alpha \int_0^{\bar{\psi}} e^{-2n\pi i \psi / \bar{\psi}} d\psi. \end{aligned} \right\} \quad (7.9)$$

Thus

$$A_3^{(0)} = \sin \alpha, \quad A_3^{(n)} = 0, \quad (n \neq 0). \quad . \quad (7.10)$$

Also

$$\begin{aligned} &B_1^{(n)} \pm i B_2^{(n)} \\ &= \mp i \bar{\psi}^{-1} \cos \alpha \int_0^{\bar{\psi}} \frac{e^{\mp i(u - q\pi)} + \tan^2 \alpha \sec (u - q\pi)}{\{1 + \tan^2 \alpha \sec^2 (u - q\pi)\}^{\frac{1}{2}}} e^{\pm i u - 2n\pi i \psi / \bar{\psi}} d\psi. \end{aligned} \quad (7.11)$$

The denominator in the integrand is

$$\begin{aligned} & \{\sec^2 \alpha + \tan^2 \alpha \tan^2 (u - q\pi)\}^{\frac{1}{2}} \\ & = \sec \alpha \{1 + \sin^2 \alpha \tan^2 (u - q\pi)\}^{\frac{1}{2}}, \end{aligned}$$

or, by (7.8), $\sec \alpha \sec (\psi - \frac{1}{2}q\bar{\psi})$,

and the remaining part of the integrand may be written in the form

$$\begin{aligned} & [1 + \tan^2 \alpha \sec (u - q\pi) \{\cos (u - q\pi) \pm i \sin (u - q\pi)\}] \\ & \quad e^{\pm q\pi i - 2n\pi i \psi / \bar{\psi}} \\ & = \sec^2 \alpha [1 \pm i \sin^2 \alpha \tan (u - q\pi)] e^{\pm q\pi i - 2n\pi i \psi / \bar{\psi}} \\ & = \sec^2 \alpha [1 \pm i \sin \alpha \tan (\psi - \frac{1}{2}q\bar{\psi})] e^{\pm q\pi i - 2n\pi i \psi / \bar{\psi}}. \end{aligned}$$

Therefore

$$\begin{aligned} & B_1^{(n)} \pm i B_2^{(n)} \\ & = \bar{\psi}^{-1} \int_0^{\bar{\psi}} \{ \mp i \cos (\psi - \frac{1}{2}q\bar{\psi}) + \sin \alpha \sin (\psi - \frac{1}{2}q\bar{\psi}) \} e^{\pm q\pi i - 2n\pi i \psi / \bar{\psi}} d\psi. \end{aligned} \quad (7.12)$$

In a similar manner we find

$$B_3^{(n)} = \bar{\psi}^{-1} \cos \alpha \int_0^{\bar{\psi}} \sin (\psi - \frac{1}{2}q\bar{\psi}) e^{-2n\pi i \psi / \bar{\psi}} d\psi. \quad (7.13)$$

In carrying out the integrations in (7.9), (7.12) and (7.13), we are to remember the different values taken by q in the range $0 < \psi < \bar{\psi}$; they may be written

$$\left. \begin{aligned} \bar{q} &= 1/3 & \text{for } 0 < \psi < \bar{\psi}/3, \\ q &= 1 & \text{for } \bar{\psi}/3 < \psi < 2\bar{\psi}/3, \\ q &= 5/3 & \text{for } 2\bar{\psi}/3 < \psi < \bar{\psi}. \end{aligned} \right\} \quad (7.14)$$

Let us make the transformation

$$\chi = \psi - \frac{1}{2}q\bar{\psi}; \quad \dots \quad (7.15)$$

then the above expressions give

$$\left. \begin{aligned} A_1^{(n)} \pm i A_2^{(n)} &= -\bar{\psi}^{-1} \cos \alpha (K^{(n)} \pm L^{(n)}) \int_{-\bar{\psi}/6}^{\bar{\psi}/6} e^{-2n\pi i \chi / \bar{\psi}} d\chi, \\ B_1^{(n)} \pm i B_2^{(n)} &= \bar{\psi}^{-1} (K^{(n)} \pm L^{(n)}) \int_{-\bar{\psi}/6}^{\bar{\psi}/6} (\mp i \cos \chi + \sin \alpha \sin \chi) \\ & \quad e^{-2n\pi i \chi / \bar{\psi}} d\chi, \\ B_3^{(n)} &= \bar{\psi}^{-1} \cos \alpha M^{(n)} \int_{-\bar{\psi}/6}^{\bar{\psi}/6} \sin \chi e^{-2n\pi i \chi / \bar{\psi}} d\chi, \\ & \dots \end{aligned} \right\} \quad (7.16)$$

where

$$\begin{aligned} K^{(n)} \pm L^{(n)} &= e^{\pm \pi i/3 - n\pi i/3} + e^{\pm \pi i - n\pi i} + e^{\pm 5\pi i/3 - 5n\pi i/3} \\ &= -\cos n\pi + 2 \cos \{(n \mp 1)\pi/3\}, \quad (7.17) \end{aligned}$$

so that

$$\left. \begin{aligned} K^{(n)} &= \cos(n\pi/3) - \cos n\pi = -2(-1)^n \sin^2(n\pi/3), \\ L^{(n)} &= \sqrt{3} \sin(n\pi/3), \end{aligned} \right\} \quad (7.18)$$

and

$$\begin{aligned} M^{(n)} &= e^{-n\pi i/3} + e^{-n\pi i} + e^{-5n\pi i/3} \\ &= 2 \cos(n\pi/3) + \cos n\pi. \end{aligned} \quad (7.19)$$

Since $K^{(0)} = L^{(0)} = 0$, the first of (7.16) gives

$$A_1^{(0)} = 0, \quad A_2^{(0)} = 0. \quad (7.20)$$

For $n \neq 0$ we have

$$A_1^{(n)} \pm iA_2^{(n)} = -\frac{\cos \alpha}{n\pi} (K^{(n)} \pm L^{(n)}) \sin(n\pi/3), \quad (7.21)$$

so that

$$\left. \begin{aligned} A_1^{(n)} &= -\frac{\cos \alpha}{n\pi} \sin(n\pi/3) \cdot K^{(n)} = -\frac{3 \cos \alpha}{2n\pi} \sin(2n\pi/3), \\ A_2^{(n)} &= \frac{i \cos \alpha}{n\pi} \sin(n\pi/3) \cdot L^{(n)} = \frac{i \sqrt{3} \cos \alpha}{2n\pi} (1 - \cos(2n\pi/3)), \\ (n &= \dots -2, -1, 1, 2, \dots). \end{aligned} \right\} \quad (7.22)$$

The second of (7.16) gives at once

$$B_1^{(0)} = 0, \quad B_2^{(0)} = 0. \quad (7.23)$$

We have

$$\begin{aligned} \psi^{-1} \int_{-\bar{\psi}/6}^{\bar{\psi}/6} (\mp i \cos \chi + \sin \alpha \sin \chi) e^{-2n\pi i \chi / \bar{\psi}} d\chi &= i(N^{(n)} \pm P^{(n)}), \\ &\dots \quad (7.24) \end{aligned}$$

where

$$\left. \begin{aligned} N^{(n)} &= \frac{2 \sin \alpha}{\psi(4n^2\pi^2/\bar{\psi}^2 - 1)} \left\{ -\cos(\bar{\psi}/6) \sin(n\pi/3) \right. \\ &\quad \left. + (2n\pi/\bar{\psi}) \sin(\bar{\psi}/6) \cos(n\pi/3) \right\}, \\ P^{(n)} &= \frac{2}{\psi(4n^2\pi^2/\bar{\psi}^2 - 1)} \left\{ \sin(\bar{\psi}/6) \cos(n\pi/3) \right. \\ &\quad \left. - (2n\pi/\bar{\psi}) \cos(\bar{\psi}/6) \sin(n\pi/3) \right\}, \end{aligned} \right\} \quad (7.25)$$

and so by (7.16)

$$B_1^{(n)} \pm iB_2^{(n)} = i(K^{(n)} \pm L^{(n)}) (N^{(n)} \pm P^{(n)}), \quad (7.26)$$

and therefore

$$B_1^{(n)} = i(K^{(n)}N^{(n)} + L^{(n)}P^{(n)}), \quad B_2^{(n)} = K^{(n)}P^{(n)} + L^{(n)}N^{(n)}. \quad (7.27)$$

The apparently formidable expressions become simpler when we substitute, by (7.6),

$$\tan(\bar{\psi}/6) = \sqrt{3} \cdot \sin \alpha. \quad (7.28)$$

We find

$$\left. \begin{aligned} B_1^{(n)} &= - \frac{i \sqrt{3} \cdot \cos^2 \alpha \cos(\bar{\psi}/6)}{\bar{\psi}} \frac{(2n\pi/\bar{\psi})(1 - \cos(2n\pi/3))}{4n^2\pi^2/\bar{\psi}^2 - 1}, \\ B_2^{(n)} &= - \frac{3 \cos^2 \alpha \cos(\bar{\psi}/6)}{\bar{\psi}} \frac{(2n\pi/\bar{\psi}) \sin(2n\pi/3)}{4n^2\pi^2/\bar{\psi}^2 - 1}. \end{aligned} \right\} \quad (7.29)$$

The above values of $B_1^{(n)}$, $B_2^{(n)}$ are valid for all integer and zero values of n .

Turning to the last of (7.16) we have

$$B_3^{(0)} = 0. \quad (7.30)$$

We have

$$\bar{\psi}^{-1} \cos \alpha \int_{-\bar{\psi}/6}^{\bar{\psi}/6} \sin \chi e^{-2n\pi i \chi / \bar{\psi}} d\chi = Q^{(n)}, \quad (7.31)$$

where

$$Q^{(n)} = \frac{2i \cos \alpha}{\bar{\psi}(4n^2\pi^2/\bar{\psi}^2 - 1)} \{ (2n\pi/\bar{\psi}) \sin(\bar{\psi}/6) \cos(n\pi/3) - \cos(\bar{\psi}/6) \sin(n\pi/3) \}, \quad (7.32)$$

and therefore

$$B_3^{(n)} = M^{(n)}Q^{(n)}. \quad (7.33)$$

On substituting from (7.28) we obtain

$$B_3^{(n)} = \frac{i \sqrt{3} \cdot \sin 2\alpha \cos(\bar{\psi}/6)}{\bar{\psi}} \frac{(2n\pi/\bar{\psi})(1 + 2 \cos(2n\pi/3))}{4n^2\pi^2/\bar{\psi}^2 - 1}. \quad (7.34)$$

The expression is valid for all integer and zero values of n .

In equations (7.10), (7.20), (7.22), (7.29), (7.34), we have evaluated explicitly the geometrical constants for an equilateral triangular root.

8. *Relations between the Applied Force System and the Displacement.*

Since the geometrical constants are fundamental in the calculations we shall collect our results here :

$$\left. \begin{aligned} A_1^{(0)} &= 0, & A_2^{(0)} &= 0, & A_3^{(0)} &= \sin \alpha, \\ A_1^{(n)} &= -\frac{3 \cos \alpha}{2n\pi} \sin (2n\pi/3), & & & & (n \neq 0), \\ A_2^{(n)} &= \frac{i\sqrt{3} \cos \alpha}{2n\pi} (1 - \cos (2n\pi/3)), & A_3^{(n)} &= 0, & & (n \neq 0), \\ B_1^{(n)} &= -\frac{i\sqrt{3} \cos^2 \alpha \cos (\bar{\psi}/6) (2n\pi/\bar{\psi}) (1 - \cos (2n\pi/3))}{\bar{\psi} 4n^2\pi^2/\bar{\psi}^2 - 1}, \\ B_2^{(n)} &= -\frac{3 \cos^2 \alpha \cos (\bar{\psi}/6) (2n\pi/\bar{\psi}) \sin (2n\pi/3)}{\bar{\psi} 4n^2\pi^2/\bar{\psi}^2 - 1}, \\ B_3^{(n)} &= \frac{i\sqrt{3} \sin 2\alpha \cos (\bar{\psi}/6) (2n\pi/\bar{\psi}) (1 + 2 \cos (2n\pi/3))}{\bar{\psi} 4n^2\pi^2/\bar{\psi}^2 - 1}. \end{aligned} \right\} \dots (8.1)$$

In these formulæ α is the inclination to the axis of the root of any one of the apical medians of its flat faces, and

$$\bar{\psi} = 6 \tan^{-1} (\sqrt{3} \cdot \sin \alpha). \dots (8.2)$$

These constants tend to zero as $1/n$. Hence the separate terms in the series (5.9) for the pressure in the membrane tend to zero as $1/n^3$, and the coefficients in the series (6.2) connecting the applied force system and the displacement of the tooth tend to zero as $1/n^4$. This convergence is satisfactory, and a few terms will suffice for approximate calculations.

We are to observe from (8.1) that $A_1^{(n)}$, $B_2^{(n)}$ are real, while $A_2^{(n)}$, $B_1^{(n)}$, $B_3^{(n)}$ are purely imaginary. Thus

$$\left. \begin{aligned} A_1^{(n)} &= A_1^{(-n)}, & A_2^{(n)} &= -A_2^{(-n)}, \\ B_1^{(n)} &= -B_1^{(-n)}, & B_2^{(n)} &= B_2^{(-n)}, & B_3^{(n)} &= -B_3^{(-n)}. \end{aligned} \right\} (8.3)$$

Equations (6.2) give the force system applied to the tooth

in terms of the resulting displacement. Let us write them in the form

$$\begin{aligned} F_j &= \nu \bar{\psi} c^4 v_k \sum_{n=0}^{\infty} R_{kj}^{(n)} + \nu \bar{\psi} c^5 \omega_k \sum_{n=0}^{\infty} S_{jk}^{(n)}, \\ G_j &= \nu \bar{\psi} c^5 v_k \sum_{n=0}^{\infty} S_{kj}^{(n)} + \nu \bar{\psi} c^6 \omega_k \sum_{n=0}^{\infty} T_{jk}^{(n)}, \end{aligned} \quad (8.4)$$

where

$$\left. \begin{aligned} R_{jk}^{(0)} &= R_{kj}^{(0)} = \frac{A_j^{(0)} A_k^{(0)}}{16}, \\ R_{jk}^{(n)} &= R_{kj}^{(n)} = \frac{A_j^{(n)} A_k^{(-n)} + A_j^{(-n)} A_k^{(n)}}{4(2 + 2n\pi/\bar{\psi})^2}, \quad (n = 1, 2, \dots), \\ S_{jk}^{(0)} &= \frac{A_j^{(0)} B_k^{(0)}}{30}, \\ S_{jk}^{(n)} &= \frac{A_j^{(n)} B_k^{(-n)} + A_j^{(-n)} B_k^{(n)}}{5(2 + 2n\pi/\bar{\psi})(3 + 2n\pi/\bar{\psi})}, \quad (n = 1, 2, \dots), \\ T_{jk}^{(0)} &= T_{kj}^{(0)} = \frac{B_j^{(0)} B_k^{(0)}}{54}, \\ T_{jk}^{(n)} &= T_{kj}^{(n)} = \frac{B_j^{(n)} B_k^{(-n)} + B_j^{(-n)} B_k^{(n)}}{6(3 + 2n\pi/\bar{\psi})^2}, \quad (n = 1, 2, \dots). \end{aligned} \right\} \quad (8.5)$$

It is easy to see from (8.1) and (8.3) that all these quantities vanish except the following:

$$\left. \begin{aligned} R_{33}^{(0)} &= \frac{(A_3^{(0)})^2}{16}, \quad R_{11}^{(n)} = \frac{(A_1^{(n)})^2}{2(2 + 2n\pi/\bar{\psi})^2}, \\ R_{22}^{(n)} &= -\frac{(A_2^{(n)})^2}{2(2 + 2n\pi/\bar{\psi})^2}, \\ S_{12}^{(n)} &= \frac{2A_1^{(n)} B_2^{(n)}}{5(2 + 2n\pi/\bar{\psi})(3 + 2n\pi/\bar{\psi})}, \\ S_{21}^{(n)} &= -\frac{2A_2^{(n)} B_1^{(n)}}{5(2 + 2n\pi/\bar{\psi})(3 + 2n\pi/\bar{\psi})}, \\ T_{11}^{(n)} &= -\frac{(B_1^{(n)})^2}{3(3 + 2n\pi/\bar{\psi})^2}, \quad T_{22}^{(n)} = \frac{(B_2^{(n)})^2}{3(3 + 2n\pi/\bar{\psi})^2}, \\ T_{33}^{(n)} &= -\frac{(B_3^{(n)})^2}{3(3 + 2n\pi/\bar{\psi})^2}, \quad (n = 1, 2, \dots). \end{aligned} \right\} \quad (8.6)$$

The vanishing of $S_{23}^{(n)}$ and $T_{13}^{(n)}$ is not seen as immediately as is the case for the other vanishing coefficients. That they vanish follows from the fact that

$$A_2^{(n)}B_3^{(n)}=0, \quad B_1^{(n)}B_3^{(n)}=0$$

for all integer values of n .

Reducing (8.4) by virtue of the vanishing of coefficients, we obtain, as the relations connecting the applied force system and the displacement for a tooth whose section is an equilateral triangle, the following equations :—

$$\left. \begin{aligned} F_1/(\nu\bar{\psi}c^4) &= v_1 \sum_{n=1}^{\infty} R_{11}^{(n)} + c\omega_2 \sum_{n=1}^{\infty} S_{12}^{(n)}, \\ F_2/(\nu\bar{\psi}c^4) &= v_2 \sum_{n=1}^{\infty} R_{22}^{(n)} + c\omega_1 \sum_{n=1}^{\infty} S_{21}^{(n)}, \\ F_3/(\nu\bar{\psi}c^4) &= v_3 R_{33}^{(0)}, \\ G_1/(\nu\bar{\psi}c^5) &= v_2 \sum_{n=1}^{\infty} S_{21}^{(n)} + c\omega_1 \sum_{n=1}^{\infty} T_{11}^{(n)}, \\ G_2/(\nu\bar{\psi}c^5) &= v_1 \sum_{n=1}^{\infty} S_{12}^{(n)} + c\omega_2 \sum_{n=1}^{\infty} T_{22}^{(n)}, \\ G_3/(\nu\bar{\psi}c^5) &= c\omega_3 \sum_{n=1}^{\infty} T_{33}^{(n)}. \end{aligned} \right\} \quad \cdot \quad \cdot \quad (8.7)$$

In these equations $\nu=12\mu/h^3$, where μ is the rigidity of the membrane, h its thickness (assumed constant), c its slant-length (assumed constant); $\bar{\psi}$ is the sum of the three (equal) angles of the faces at the apex given in terms of α by (7.28), where α is the inclination to the axis of the root of any one of the apical medians of the faces; the quantities $R_{jk}^{(n)}$, $S_{jk}^{(n)}$, $T_{jk}^{(n)}$ are certain constants depending only on α and n , given by (8.6) and (8.1).

Certain simple types of force systems are of interest. Under a purely axial load, defined by

$$F_1=F_2=0, \quad F_3=-F, \quad G_1=G_2=G_3=0, \quad \cdot \quad (8.8)$$

the displacement has only one component,

$$v_3 = -\frac{F}{\nu\bar{\psi}c^4 R_{33}^{(0)}} = -\frac{4Fh^3}{3\mu\bar{\psi}c^4 \sin^2 \alpha} \quad \cdot \quad \cdot \quad (8.9)$$

Let the tooth receive a transverse load at the biting edge, which we shall assume to be at a distance ρ from the apex, the force system being

$$F_1=-F, \quad F_2=F_3=0, \quad G_1=0, \quad G_2=-\rho F, \quad G_3=0. \quad \cdot \quad \cdot \quad (8.10)$$

We have then from (8.7)

$$v_2 = v_3 = \omega_1 = \omega_3 = 0,$$

and

$$\left. \begin{aligned} v_1 \sum_{n=1}^{\infty} R_{11}^{(n)} + c\omega_2 \sum_{n=1}^{\infty} S_{12}^{(n)} &= -F/(\nu\bar{\psi}c^4), \\ v_1 \sum_{n=1}^{\infty} S_{12}^{(n)} + c\omega_2 \sum_{n=1}^{\infty} T_{22}^{(n)} &= -\rho F/(\nu\bar{\psi}c^5). \end{aligned} \right\} \quad (8.11)$$

Therefore the surviving components of displacement are

$$\left. \begin{aligned} v_1 &= \frac{F}{\nu\bar{\psi}c^4} \frac{(\rho/c) \sum_{n=1}^{\infty} S_{12}^{(n)} - \sum_{n=1}^{\infty} T_{22}^{(n)}}{\left(\sum_{n=1}^{\infty} R_{11}^{(n)} \right) \left(\sum_{n=1}^{\infty} T_{22}^{(n)} \right) - \left(\sum_{n=1}^{\infty} S_{12}^{(n)} \right)^2}, \\ \omega_2 &= -\frac{F}{\nu\bar{\psi}c^5} \frac{(\rho/c) \sum_{n=1}^{\infty} R_{11}^{(n)} - \sum_{n=1}^{\infty} S_{12}^{(n)}}{\left(\sum_{n=1}^{\infty} R_{11}^{(n)} \right) \left(\sum_{n=1}^{\infty} T_{22}^{(n)} \right) - \left(\sum_{n=1}^{\infty} S_{12}^{(n)} \right)^2}. \end{aligned} \right\} \quad (8.12)$$

Accordingly the tooth turns about an axis whose equations are

$$y_1 = 0, \quad y_3 = b, \quad . \quad . \quad . \quad . \quad (8.13)$$

where

$$b = -\frac{v_1}{\omega_2} = c \frac{(\rho/c) \sum_{n=1}^{\infty} S_{12}^{(n)} - \sum_{n=1}^{\infty} T_{22}^{(n)}}{(\rho/c) \sum_{n=1}^{\infty} R_{11}^{(n)} - \sum_{n=1}^{\infty} S_{12}^{(n)}}. \quad (8.14)$$

This distance b may be referred to as the distance of the centre of rotation from the apex under the action of a purely transverse load at distance ρ . A numerical result will be found in (10.7).

Let us now suppose that the tooth is subject only to a torque G about the axis of the root. We have then

$$F_1 = F_2 = F_3 = 0, \quad G_1 = G_2 = 0, \quad G_3 = G, \quad . \quad (8.15)$$

and hence there is only one component of displacement,

$$\omega_3 = \frac{G}{\nu\bar{\psi}c^6 \sum_{n=1}^{\infty} T_{33}^{(n)}}. \quad . \quad . \quad . \quad (8.16)$$

This may be regarded as the solution (as far as the displacement of the tooth is concerned) of the torsion problem for a tooth whose cross-section is an equilateral triangle.

9. The Pressure Distribution.

For the pressure distribution in the membrane we turn to (5.9). Using (8.3) and (8.1) we have

$$\begin{aligned}
 p = P + \frac{\nu c^2}{4} \left\{ \left(\frac{r}{c} \right)^2 - 1 \right\} v_3 \sin \alpha \\
 + 2\nu c^2 \sum_{n=1}^{\infty} \frac{(r/c)^2 - (r/c)^{2n\pi/\bar{\psi}}}{4 - (2n\pi/\bar{\psi})^2} \{ v_1 A_1^{(n)} \cos (2n\pi\psi/\bar{\psi}) \\
 + i v_2 A_2^{(n)} \sin (2n\pi\psi/\bar{\psi}) \} \\
 + 2\nu c^3 \sum_{n=1}^{\infty} \frac{(r/c)^3 - (r/c)^{2n\pi/\bar{\psi}}}{9 - (2n\pi/\bar{\psi})^2} \{ i \omega_1 B_1^{(n)} \sin (2n\pi\psi/\bar{\psi}) \\
 + \omega_2 B_2^{(n)} \cos (2n\pi\psi/\bar{\psi}) + i \omega_3 B_3^{(n)} \sin (2n\pi\psi/\bar{\psi}) \}. \quad (9.1)
 \end{aligned}$$

This is the general expression for the pressure distribution when the cross-section of the root is an equilateral triangle. The constants have been described in the preceding section. Here r, ψ are polar coordinates in the plane development of the root.

Under a purely axial load, given by (8.8), the pressure distribution is

$$p = P + \frac{4F(c^2 - r^2)}{\psi c^4 \sin \alpha} \quad \dots \quad (9.2)$$

The pressure at the apex is

$$p = P + \frac{4F}{\psi c^2 \sin \alpha}, \quad \dots \quad (9.3)$$

and the critical axial load, namely, that pull required to reduce the pressure at the apex to zero, is of magnitude

$$\frac{1}{4} P c^2 \bar{\psi} \sin \alpha, \quad \dots \quad (9.4)$$

P being the atmospheric pressure.*

* In the paper referred to in § 1 I obtained for the critical axial load, in the case of a root in the form of a right circular cone, the value $\frac{1}{3}AP$, where A is the area of the cross-section of the root at the edge of the membrane. It is easily seen that the expression (9.4) is approximately $\frac{1}{2}AP$ when the root is very sharp.

For a transverse load, defined by (8.10), the displacement is given by (8.12), and, in terms of the displacement, the pressure distribution is

$$p = P + 2\nu c^2 \sum_{n=1}^{\infty} \left\{ \frac{(r/c)^2 - (r/c)^{2n\pi/\bar{\psi}}}{4 - (2n\pi/\bar{\psi})^2} v_1 A_1^{(n)} + \frac{(r/c)^3 - (r/c)^{2n\pi/\bar{\psi}}}{9 - (2n\pi/\bar{\psi})^2} c\omega_2 B_2^{(n)} \right\} \cos(2n\pi\bar{\psi}/\bar{\psi}). \quad (9.5)$$

In carrying out this summation all terms for which n is a multiple of 3 may be omitted, because for such values $A_1^{(n)}$ and $B_2^{(n)}$ vanish. We observe that the pressure is atmospheric at the apex.

Under the torsional load (8.15) we have

$$p = P + 2\nu c^3 \sum_{n=1}^{\infty} \frac{(r/c)^3 - (r/c)^{2n\pi/\bar{\psi}}}{9 - (2n\pi/\bar{\psi})^2} i\omega_3 B_3^{(n)} \sin(2n\pi\bar{\psi}/\bar{\psi}). \quad (9.6)$$

But by (8.1) $B_3^{(n)}$ vanishes unless n is a multiple of 3. Thus we have, in terms of the torque G , by (8.16),

$$p = P + kGc^{-3} \sum_{m=1}^{\infty} V^{(m)} \left\{ (r/c)^3 - (r/c)^{6m\pi/\bar{\psi}} \right\} \sin(6m\pi\bar{\psi}/\bar{\psi}), \quad (9.7)$$

where k depends only on α , being

$$k = \frac{2}{\bar{\psi} \sum_{n=1}^{\infty} T_{33}^{(n)}}, \quad (9.8)$$

and

$$\begin{aligned} V^{(m)} &= \frac{iB_3^{(3m)}}{9 - (6m\pi/\bar{\psi})^2} \\ &= \frac{3\sqrt{3} \cdot \sin 2\alpha \cos(\bar{\psi}/6)}{\bar{\psi}} \frac{6m\pi/\bar{\psi}}{\{(6m\pi/\bar{\psi})^2 - 1\} \{(6m\pi/\bar{\psi})^2 - 9\}}. \end{aligned} \quad (9.9)$$

We note that the pressure is atmospheric at the apex and along each of the edges, $\bar{\psi} = 0$, $\bar{\psi} = \bar{\psi}/3$, $\bar{\psi} = 2\bar{\psi}/3$. It is also atmospheric along each of the apical medians.

10. Some Numerical Results.

As remarked in § 1, the results of a mathematical investigation of a physiological problem such as the present one cannot claim a high degree of quantitative accuracy. It

seems profitable, however, to extract some numerical values from the preceding results by inserting for the constants values which agree approximately with actual measurements. The fundamental constants and the values which we shall assign to them are as follows :—

$$\left. \begin{array}{l} \text{Inclination of axis of root to any one of the apical} \\ \text{medians of the flat faces} = \alpha = 8^\circ, \\ \text{Length of membrane measured along the gene-} \\ \text{rators and assumed constant} = c = 16 \text{ mm.}, \\ \text{Distance from apex to biting edge} = \rho = 3c/2. \end{array} \right\} (10.1)$$

From the value of α we deduce

$$\left. \begin{array}{l} \bar{\psi} = 6 \tan^{-1} (\sqrt{3} \cdot \sin \alpha) = 81^\circ 18' = 1.419 \text{ radians}, \\ \bar{\psi}/6 = 13^\circ 33', \quad 2\pi/\bar{\psi} = 4.428. \end{array} \right\} (10.2)$$

Formulae (8.1) then yield the following numerical values for the geometrical constants, which, of course, depend on α only, and not on c or ρ :—

$$\left. \begin{array}{lll} A_1^{(0)} = 0, & A_2^{(0)} = 0, & A_3^{(0)} = 0.1392, \\ A_1^{(1)} = -0.410, & A_2^{(1)} = 0.410i, & A_3^{(1)} = 0, \\ A_1^{(2)} = 0.205, & A_2^{(2)} = 0.205i, & A_3^{(2)} = 0, \\ A_1^{(3)} = 0, & A_2^{(3)} = 0, & A_3^{(3)} = 0, \\ A_1^{(4)} = -0.1025, & A_2^{(4)} = 0.1025i, & A_3^{(4)} = 0, \\ A_1^{(5)} = 0.082, & A_2^{(5)} = 0.082i, & A_3^{(5)} = 0, \\ A_1^{(6)} = 0, & A_2^{(6)} = 0, & A_3^{(6)} = 0; \end{array} \right\} (10.3)$$

$$\left. \begin{array}{lll} B_1^{(0)} = 0, & B_2^{(0)} = 0, & B_3^{(0)} = 0, \\ B_1^{(1)} = -0.415i, & B_2^{(1)} = -0.415, & B_3^{(1)} = 0, \\ B_1^{(2)} = -0.200i, & B_2^{(2)} = 0.200, & B_3^{(2)} = 0, \\ B_1^{(3)} = 0, & B_2^{(3)} = 0, & B_3^{(3)} = 0.0743i, \\ B_1^{(4)} = -0.099i, & B_2^{(4)} = -0.099, & B_3^{(4)} = 0, \\ B_1^{(5)} = -0.079i, & B_2^{(5)} = 0.079, & B_3^{(5)} = 0, \\ B_1^{(6)} = 0, & B_2^{(6)} = 0, & B_3^{(6)} = 0.0370i, \\ & & B_3^{(9)} = 0.0246i, \\ & & B_3^{(12)} = 0.0185i. \end{array} \right\} (10.4)$$

Hence we find from (8.6)

$$\sum_{n=1}^{\infty} R_{11}^{(n)} = 0.00223, \quad \sum_{n=1}^{\infty} S_{12}^{(n)} = 0.00157, \quad \sum_{n=1}^{\infty} T_{22}^{(n)} = 0.00115. \quad (10.5)$$

Equation (8.14) gives for the distance of the centre of rotation from the apex, when a transverse force is applied at a distance ρ from the biting edge,

$$b = c \frac{157(\rho/c) - 115}{223(\rho/c) - 157}, \quad (10.6)$$

or, using the value of ρ given in (10.1),

$$b = 0.679c. \quad (10.7)$$

We may therefore state that, *under the action of a transverse force applied at the biting edge, the centre of rotation is distant from the apex about two-thirds of the root-length**.

Let us now investigate the numerical significance of the torsion result given in (8.16). We find

$$\sum_{n=1}^{\infty} T_{33}^{(n)} = 7.62 \times 10^{-6}, \quad \frac{1}{\psi \sum_{n=1}^{\infty} T_{33}^{(n)}} = 9.25 \times 10^4. \quad (10.8)$$

Then (8.16) gives for the rotation produced by a couple G about the axis of the tooth

$$\omega_3 = 9.25 \times 10^4 G / (\nu c^6) = 7.71 \times 10^3 G h^3 / (\mu c^6), \quad (10.9)$$

where μ is the rigidity and h the thickness of the membrane. To get an idea of the magnitude of this quantity let us take

$$\left. \begin{aligned} h &= 0.24 \text{ mm.}, \\ \mu &= 1.6 \times 10^7 \text{ dynes cm.}^{-2} = 1.63 \times 10^2 \text{ gm. mm.}^{-2}, \end{aligned} \right\} \quad (10.10)$$

this value of μ being that of rubber. These numerical values give

$$\omega_3 = 3.90 \times 10^{-8} G, \quad (10.11)$$

where G is expressed in gm.mm. and ω_3 in radians. The torque required to twist the tooth through 0.1° is therefore about 4500 gm. mm. It is to be remembered that the value

* In the paper referred to in §1 I obtained for this distance, in the case of a right-circular conical root, nearly three-quarters of the root-length. A different value of ρ/c was employed, but (10.6) is not sensitive to small changes in ρ/c .

of μ here assumed (for this special result) is quite tentative: the rigidity of the membrane may be very different from that of rubber.

Let us now consider the pressure distribution. We shall confine our attention to the simplest case, namely, that of pure twisting, for which the pressure is given by (9.7). We find, from (9.8) and (10.8),

$$k = 1.850 \times 10^5; \quad . \quad . \quad . \quad . \quad (10.12)$$

the values of $V^{(m)}$ may be calculated from (9.9) and (10.2), and we get, on substitution in (9.7),

$$\begin{aligned} p = P + Gc^{-3} [& 82.10 \{ (r/c)^3 - (r/c)^{13.28} \} \sin (6\pi\psi/\bar{\psi}) \\ & + 9.82 \{ (r/c)^3 - (r/c)^{26.56} \} \sin (12\pi\psi/\bar{\psi}) \\ & + 2.89 \{ (r/c)^3 - (r/c)^{39.84} \} \sin (18\pi\psi/\bar{\psi}) \\ & + 1.21 \{ (r/c)^3 - (r/c)^{53.12} \} \sin (24\pi\psi/\bar{\psi}) \\ & + 0.62 \{ (r/c)^3 - (r/c)^{66.41} \} \sin (30\pi\psi/\bar{\psi}) \\ & + 0.36 \{ (r/c)^3 - (r/c)^{79.69} \} \sin (36\pi\psi/\bar{\psi}) \\ & + 0.23 \{ (r/c)^3 - (r/c)^{92.97} \} \sin (42\pi\psi/\bar{\psi}) \\ & + 0.15 \{ (r/c)^3 - (r/c)^{106.3} \} \sin (48\pi\psi/\bar{\psi}) \\ & + 0.11 \{ (r/c)^3 - (r/c)^{119.6} \} \sin (54\pi\psi/\bar{\psi}) \\ & + \dots] . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.13) \end{aligned}$$

This is the pressure distribution in the membrane of a tooth of equilateral triangular section (the flat faces being inclined to the axis of the root at an angle of 8°) when the tooth is twisted by a couple G about its axis.

The pressure distribution is, of course, the same on each of the faces. The pressure, as remarked earlier, is atmospheric on the edges and on the apical medians of the faces, whose apical angles are $\bar{\psi}/3$. The points of maximum and minimum pressure are given by

$$\partial p / \partial r = 0, \quad \partial p / \partial \psi = 0. \quad . \quad . \quad . \quad (10.14)$$

Using the first term only of the series in (10.13) we find for the points of maximum and minimum pressure on the face $0 < \psi < \bar{\psi}/3$, assuming $G > 0$,

$$\begin{aligned} r/c = 0.865, \quad \psi = \bar{\psi}/12; \quad r/c = 0.865, \quad \psi = \bar{\psi}/3 - \bar{\psi}/12 \\ . \quad . \quad . \quad (10.15) \end{aligned}$$

respectively. A second approximation gives

$$\left. \begin{aligned} r/c &= 0.867, & \psi &= 0.810\bar{\psi}/12; \\ r/c &= 0.867, & \psi &= \bar{\psi}/3 - 0.810\bar{\psi}/12. \end{aligned} \right\} \quad (10.16)$$

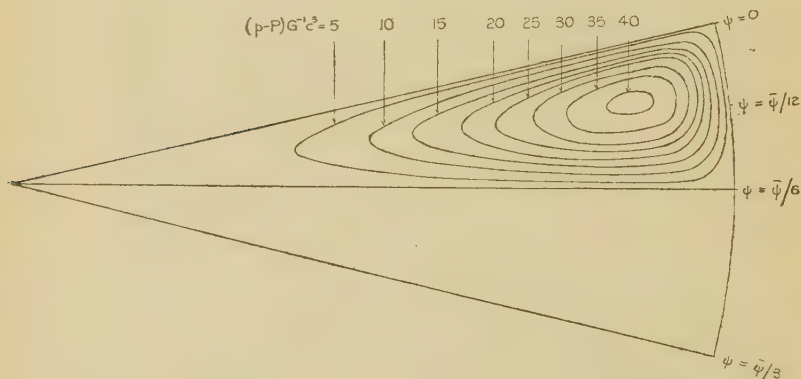
The pressures at these points are found to be respectively

$$p = P \pm 41.1 Gc^{-3} \quad . \quad . \quad . \quad (10.17)$$

for any units, and hence the *critical torque*, which raises the pressure to two atmospheres at the points of maximum pressure and reduces it to zero at the points of lowest pressure, is

$$G = Pc^3/41.1 = 1030 \text{ gm. mm.}, \quad . \quad . \quad (10.18)$$

Fig. 4.



when P is one atmosphere (1.013×10^6 dynes cm.^{-2} or 10.33 gm.mm. $^{-2}$).

Fig. 4 shows the lines of constant pressure on one half of one of the faces of the root. The torque G tends to turn the upper edge of the face towards us. The lines on the other half of the face are the images of the drawn lines with respect to the line $\psi = \bar{\psi}/6$, and the value of $(p-P)G^{-1}c^3$ corresponding to any one of these image lines has the same absolute value as, and the opposite sign to, the value corresponding to the drawn line.

I have to thank my colleague, Mr. B. A. Griffith, for assistance in checking the calculations.

LXXVIII. *Crookes's Radiometer and the Intensity of Radiation.* By G. RUSSELL, *University College, Exeter* *.

1. *Introduction.*

IT was suggested by Crookes that his well-known radiometer might be used as a photometer, the speed of rotation of the vanes being proportional to the intensity of the incident radiation. Thus, assuming that the time for one complete revolution is T and that the radiation source is at a distance d from the radiometer, Crookes found that $d^2 = kT$ where k is a constant of the instrument. Since the intensity of the incident radiation varies inversely as d^2 he concluded that the apparatus could be employed to measure the intensity of the radiation.

Although his experimentally determined values of d and T satisfied the above relationship, the agreement for small values of these variables was not so satisfactory as for large values, the speeds being less in proportion than the corresponding values of $1/d^2$. This suggests that either for great speeds the rate of rotation of the vanes is not proportional to the radiation, or, that for such small distances the radiation from his source (a candle) was not proportional to $1/d^2$.

Radiometer phenomena have been explained by several investigators including Schuster †, Osborne Reynolds ‡, Rayleigh §, and West ||. For the explanation of such phenomena there are two types of friction to be considered, (*a*) that at the pivot, and (*b*) that due to the residual gas within the vessel. Experiment shows that the rate of revolution of the vanes soon reaches a steady value for a particular source of radiation at a fixed distance from the instrument, and thus the "gas friction" is proportional to the speed, even up to the high speeds obtained in the instrument.

Now if F represents the friction at the pivot, N the number of revolutions per minute (R.P.M.), kN the friction due to the gas, I the power of the radiation

* Communicated by Professor F. H. Newman, D.Sc.

† Phil. Trans. clx. p. 715 (1876).

‡ *Ibid.* clxvi. p. 725 (1876).

§ 'Nature,' lxxxi. p. 69 (1909).

|| Proc. Phys. Soc. xxxi. p. 278; xxxii. p. 166 (1919).

source at a distance d from the radiometer, and if we assume that the radiation is incident normally upon the vanes,

$$I/d^2 = F + kN,$$

so that if d_0 is the value of d when the rotation just ceases,

$$I/d_0^2 = F,$$

or,

$$I/d^2 = I/d_0^2 + kN.$$

Therefore, if $1/d^2$ be plotted against N , the graph should be a straight line which does not pass through the origin of coordinates unless the friction at the pivot is zero.

Satterly * has used the radiometer to measure the radiation at different distances from a red-hot iron sphere. Plotting values of $1/d^2$ against R.P.M. (number of revolutions of the vanes per minute), his results showed that the graph was practically straight and passed through the origin, except for speeds less than 5 to 7 R.P.M. (for the particular instrument used). At speeds less than these the R.P.M. fell off more quickly than the intensity, and for a certain low value of the intensity the vanes did not rotate at all. His results differed from those of Crookes both for small and large distances. In one particular case the equation of the curve was

$$1/d^2 = 0.000025 N + 0.000075 \times 10^{-18} N,$$

but there appears to be no special meaning to the exponential term, and no explanation was advanced for the departure from the linear law.

2. Experimental.

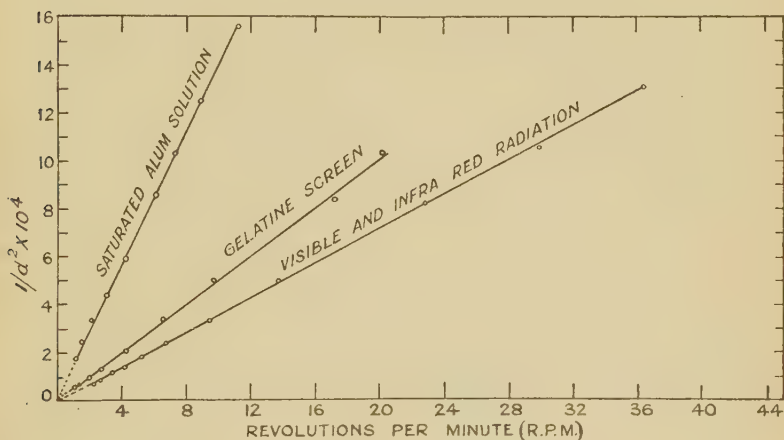
During some experiments on the measurement of daylight factors the application of the radiometer as a photometer was considered, and the variation of the rate of revolution of the vanes with the intensity of visible and infra-red radiation was examined. The experiments were carried out in a special photographic room, the radiometer being enclosed in a glass container to minimise the effect of air convection currents in the room upon the instrument. The source of radiation, an electric lamp enclosed in a blackened container, and radiometer were arranged on a photometer bench. Both A.C. and

* Trans. Roy. Soc. Canada, xvi. p. 75 (1922).

D.C. sources of electrical supply were used, but the nature of the supply appeared to have no effects upon the measurements. Distances were measured from the lamp filament to a point $(\sqrt{3}-1)l/2$ in front of the axis of the radiometer, where l is the length of the arm of the vane.

In the first series of experiments the lamp was placed at different distances from the instrument and the number of revolutions per minute determined. For comparatively great distances several observations of the time required for five revolutions were made, a fixed time-interval being allowed between each observation. With small distances

Fig. 1.

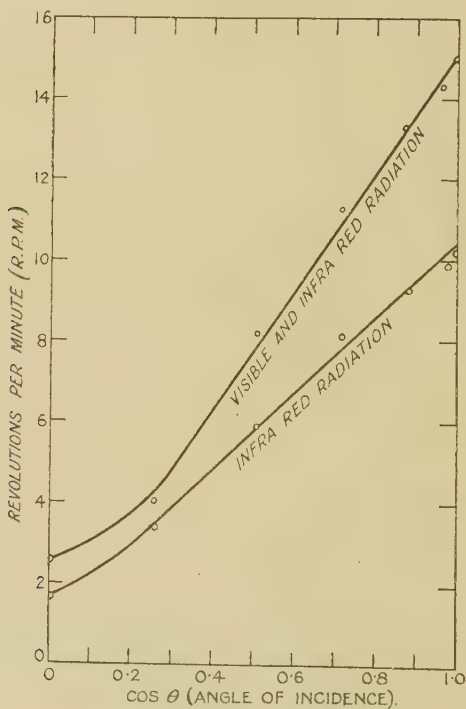


the time for fifty revolutions was observed, but before taking any observation the instrument was allowed to remain in total darkness for five minutes, and after starting the radiation, the vanes were permitted to run for two minutes before the timing was started.

Three sets of observations were made, viz., (a) full radiation from the lamp; (b) a cell containing a saturated solution of alum was inserted between the lamp and the radiometer, so that most of the infra-red radiation was absorbed; (c) a gelatine screen cutting off the visible radiation was interposed between the lamp and radiometer. The results obtained in these three cases are shown in fig. 1. It will be noted that the graphs are straight lines over the greater part of their paths, and

it is only for comparatively large distances that there is a slight departure from this linear relationship. The lines pass through the origin, so that the friction at the pivot must be extremely small compared with that due to the residual air. These results are similar to those obtained by Satterly. The absence of appreciable pivot friction was also indicated by the fact that a slow

Fig. 2.



rotation of the vanes occurred however feeble the intensity of the radiation. The only differences between the curves for visible and infra-red radiation are to be found in the different slopes, the infra-red radiation being more effective in promoting rotation of the vanes than the visible radiation.

In a second series of experiments the lamp was kept at a constant distance from the radiometer and the rate of rotation measured as the angle of incidence of the

radiation upon the vanes was altered, the lamp and radiometer always being in the same vertical plane with the lamp directed towards the radiometer. The revolutions per minute were plotted against the cosine of the angle of incidence, and the results obtained are shown in fig. 2. The graphs are straight lines over the greater part of their length, but depart from this linear condition near the origin, *i. e.*, when the source of radiation is vertically above the radiometer. In this position the angle of incidence is not equal to 90° for the four vanes, so that there is, as would be expected, a rotation of the vanes corresponding to this position, *viz.*, $\theta = 90^\circ$. It will be noted that the straight lines do not pass through the origin of coordinates.

The results of these experiments indicate that the rate of revolution of the vanes is directly proportional to the intensity of the incident radiation, this intensity varying inversely as the square of the distance and directly as the cosine of the angle of incidence.

The above work was carried out under the direction of Prof. Newman.

LXXIX. *Structure of Cyanuric Triazide* (C_3N_3)(N_3)₃. By
T. CARLTON SUTTON, *M.Sc., F.Inst.P., Research Department, Royal Arsenal, Woolwich* *.

[Plates XIX. & XX.]

Introduction.

THE constituent atoms of cyanuric triazide, carbon and nitrogen, differ in atomic number by one unit. So small a difference is rare among organic crystals. Conditions are favourable, therefore, for a solution of the crystal structure in which the position on the lattice of every atom in the crystal is determined.

I. Measured properties of the crystal are detailed in sections 1 to 8.

II. From the crystal shape and some simple X-ray diffractions the size of the elementary cell is deduced in section 9.

* Communicated by the Author.

III. Arguments are then put forward by means of which a position on the lattice is found for each of the thirty atoms of the minimum elementary cell:—

- (i.) It is shown that the crystal may be regarded as a number of hexagonal prisms (sections 11 and 12), and that the prism edges are formed by chains of atoms (section 13). Some explanation is required for the great distance, $2.89 \text{ \AA}$., between these parallel chains, a distance approximately four times the radius of the nitrogen atom, $0.73 \text{ \AA}$.
- (ii.) It is shown in section 14 that when three carbon and three nitrogen atoms are arranged in sextet rings in the same way as the six carbon atoms in the sextet ring of benzene, their size is such that, when placed normal to the axes of the prisms, these rings fit within and completely fill the prisms, thus supplying a mechanism for fixing the apparently arbitrary distance $2.89 \text{ \AA}$.
- (iii.) From the symmetry of the crystal, the position of these sextet rings in the unit elementary cell is determined in section 15.
- (iv.) From the symmetry of the crystal and the known size and number of the nitrogen atoms, the positions of these atoms on the edges of the hexagonal prisms is determined in section 16.

IV. From the evidence thus obtained in Part III., a complete atomic model may be constructed as in section 17

The properties derived from such a model are compared with the measured properties of the crystal in Tables III. and IV., and are found to agree within the limits of measurement.

In view of the deductions made in Part III. and the agreement shown in Tables III. and IV., the structure of the model is (section 18) evidence that, in the case of cyanuric azide,

- (i.) The molecules crystallize as typical organic molecules.
- (ii.) The azide group is a short chain of three nitrogen atoms linked to the cyanuric ring by the middle nitrogen.

- (iii.) The effective diameter of ring nitrogen is substantially the same as that of chain nitrogen.
- (iv.) The cyanuric group resembles the benzene group and consists of a hexagonal ring of six atoms, so arranged that the centres of neighbouring atoms are $1.44 \text{ \AA}$. apart, *i. e.*, the (spheres of influence of) neighbouring atoms are in contact.

Part I.—DATA.

Crystal Shape.

1. Satisfactory crystals* were obtained from solutions in acetone and from solutions in methyl ethyl ketone.

The habit is that of a holohedral hexagonal prism, terminated by a single hexagonal pyramid. Basal planes, secondary prisms, and secondary pyramids are conspicuously absent. The simple form is well and regularly developed.

[A tabular habit, noticed in a few cases, was due to the growth of two parallel prism-planes, and occurred when crystallization took place from layers of liquid not exceeding one-half centimetre in depth.]

The crystals used for the following determinations were slender, small, six-sided prisms with pyramidal terminations. Their average length was about 3 mm., their breadth about $\frac{1}{2}$ mm.

They were transparent and, although mainly colourless, some showed a delicate pale pink coloration.

The crystal faces were brilliant when freshly made, but dulled on exposure on account of evaporation. The fresher and brighter crystals gave good reflexions on the goniometer.

Measurements of the prism-zone showed a 60° prism.

The measurements are consistent one with another, and show the crystal to be of the form summarized in the stereographic projection detailed in diagram 1 (Pl. XIX.)

The best measurements were made with a crystal of about 2 mm. length and $\frac{1}{3}$ mm. breadth, in the zone $m_1p_1p_4m_1$ and corresponding zones.

Two excellent readings, $51^\circ 41\frac{1}{2}'$ and $51^\circ 42'$, were obtained for the angle between prism and pyramid.

* The material was made by Mr. H. Whittaker, M.Sc.

These readings agree within one-half of one minute, and were so much better than some of the other readings*, that their mean has been taken to give the best value of Miller's element, $38^{\circ} 18' 15''$. From this the value 0.684 is obtained for the axial ratio.

The following check measurements of the angles between various faces were made:—

TABLE I.

Faces.	Angle between faces.	
	Measured.	Calculated (axial ratio 0.684).
p_1 and m_2	$71^{\circ} 58' 30''$	$71^{\circ} 56' 45''$
m_1 „ m_2	$60^{\circ} 0' 0''$	$60^{\circ} 0' 0''$
m_1 „ p_1	$51^{\circ} 41' 45''$	$51^{\circ} 41' 45''$
p_1 „ p_4	$76^{\circ} 31' 30''$	$76^{\circ} 36' 30''$
p_2 „ m_3	$71^{\circ} 58' 30''$	$71^{\circ} 56' 45''$
p_1 „ p_3	$35^{\circ} 56' 0''$	$36^{\circ} 6' 30''$

Etched Figures.

2. Fine lines parallel to the principal axis were obtained on etching the prism faces. These etched figures were placed similarly on each of the faces and symmetrically with respect to the equatorial planes.

Optical Properties.

3. The crystals gave uniformly straight extinction. The following values were found for the refractive indices:—

- (i.) Light vibrating parallel to the principal axis (extraordinary ray)

$$\lambda=5791, \mu=1.378(3); \lambda=5461, \mu=1.380(5).$$

- (ii.) Light vibrating normal to the principal axis (ordinary ray)

$$\lambda=5791, \mu=1.862(4); \lambda=5461, \mu=1.871(7).$$

* Six less good readings in these zones, with a maximum difference of $19'$ for the angle between prism and pyramid, gave a mean of $51^{\circ} 41' 15''$, i. e. differing by $30''$ from the value adopted.

The crystal is thus optically negative, the birefringence has the high value 0.49, and the dispersive power for the ordinary ray is large.

The absorption and pleochroic scheme is "O (pale pink) greater than E (colourless)."

The crystals fluoresce in the light from a mercury vapour lamp.

Owing to the explosive character of the substance, there is a difficulty in obtaining a section of a crystal cut normally to the optic axis. It has been impossible, therefore, to obtain an axial convergent light figure whereby the uniaxial character of the substance could have been further tested.

Planes of Cleavage.

4. Planes of cleavage were sought, particularly at right angles to the principal axis. Although the crystals broke easily and divided into smaller crystals, no cleavage plane was observed.

Chemistry.

5. There is complete agreement among chemists that the formula for cyanuric triazide should be written $(C_3N_3)(N_3)_3$, where (C_3N_3) is the cyanuric ring* consisting of alternate atoms of carbon and of nitrogen, and N_3 is the azide grouping. The structure of the azide group (N_3) is, however, still under discussion†. While, in the cases of a number of liquid azides, the balance of evidence is in favour of the ring formula‡ of fig. 1 (p. 1006), examination of the crystals§ of sodium and of potassium

* James Walker and others, J. C. S. lxvii. (1895) *et seq.*; E. A. Werner and others, J. C. S. ciii. (1913) *et seq.*; Werner and Fearon, J. C. S. cxvii. p. 1356; E. A. Werner, 'Chemistry of Urea,' p. 17 *et seq.*

† Curtius, *Ber.* xxiii. p. 3023 (1890); Thiele, *Ber.* xlv. p. 2523 (1911); Staudinger, *Helv. Chim. Acta*, iv. p. 213 (1921), v. p. 75 (1922); Angeli, *Atti R. Acc. Lincei*, lxx. p. 732 (1926); Mendeljeff, 'Principles of Chemistry,' ii. p. 455; Browne and Wilcoxon, J. A. C. S. xlviii. p. 682 (1926); Wislicenus, *Ber.* xxv. p. 2084 (1892); Philip, J. C. S. xciii. p. 918 (1908), ci. p. 1866 (1912); Lindemann and Thiele, *Ber.* lxi. p. 1529 (1928); Gotsky, *Ber.* lxiv. p. 1555 (1931); Sugden, 'Parachor and Valency,' p. 123; Forster and Newman, J. C. S. xcvii. p. 2572 (1910); Sidgwick, J. C. S. 1929, p. 1108.

‡ L. E. Sutton, 'Nature,' Oct. 9, 1931, p. 639.

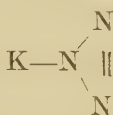
§ Hendricks and Pauling, J. A. C. S. xlvii. p. 2390 (1925).

azide has led, in each case, to the placing of the nitrogen atoms in a short chain*.

On analogy with the constitution of cyanuric chloride†, from which cyanuric azide may be prepared, the azide groups would be linked to the carbon atoms of the cyanuric ring. In the absence of direct work with the azide itself, however, the possibility of linkage to the nitrogen atoms of the ring should not be disregarded.

Whichever view is taken, the azide groups are linked to alternate atoms of the cyanuric ring.

Fig. 1.



Mass of the Molecule.

6. Measurements have been made of the freezing-points of solutions of cyanuric azide in benzene. The molecular weights deduced from these measurements varied from 209 to 199. Within the limits of measurement, these values agree with the molecular weight 204 of the simple non-associated molecule $(\text{C}_3\text{N}_3)(\text{N}_3)_3$. The mass of such a molecule is 3.35×10^{-22} grams.

Radiology.

7. Some measurements with an ionization spectrometer of the original Bragg type are given in Table II. These have included diffractions from the three main planes of the crystal.

Density of the Crystal.

8. A crop of crystals was immersed in a solution of potassium mercury iodide in alcohol. The system was then connected to an exhaust pump, and the density of the liquid gradually increased by evaporation until the crystals floated.

* T. C. Sutton, 'Nature,' Nov. 21, 1931, p. 872.

† Chattaway, J. C. S. lxxxi. p. 191 (1902).

Several of the crystals were found to contain air-holes and cavities filled with solvent. Such crystals are detected by the way they float, having a particular side uppermost and swaying slowly to and fro about a position of equilibrium; they have spuriously low densities.

Ninety per cent. of the crop, however, gave a regular result corresponding with a density of 1.71.

TABLE II.

X-ray Diffractions from Crystal of Cyanuric Triazide.

Plane.	Spacings (Ångström units).	Approx. intensity.
(0001)	2.97	45
	1.48	400
(10 $\bar{1}$ 0)	7.56	20 (?)*
	2.52	35
	1.26	20
(1 $\bar{2}$ 10)	4.33	45
	2.17	25
	1.44	15
(1 $\bar{2}$ 11)	4.92	160
	2.46	trace
	1.64	trace
(10 $\bar{1}$ 1)	4.70	170
	2.35	trace
	1.57	trace

* Close to central beam.

Part II.—DIMENSIONS OF THE MINIMUM ELEMENTARY CELL.

9. X-ray diffractions from the plane normal to the principal axis (0001) are recorded in Table II. These show that the spacings between layers of atoms are 1.48 Å. or 2.97 Å. The unit distance along the principal axis is therefore $2.97n$, where n is a small integer. The crystal measurements have shown that the axial ratio is 0.684. It follows from these values that the volume of the minimum elementary cell is $4.87 \times 10^{-33} \times n^3$ c.c. Since

the density of the crystal is 1.71, the mass of the cell is therefore $8.32 \times 10^{-23} n^3$ grams. As the cell contains a whole number (N) of molecules, its mass may also be expressed as a multiple of the molecular mass (section 6), *i.e.*, as $3.35 \times 10^{-22} N$ grams. For these two expressions to be equal, $4N = n^3$, n and N being integers, N may therefore have the values 2, 16, 54, 128... etc., the corresponding values of n being 2, 4, 6, 8... etc. Since the minimum elementary cell is the smallest volume which completely determines the form of the crystal, the smallest values consistent with the measurements are taken, namely, $N = n = 2$. Hence,

- (a) The unit distance along the principal axis is twice the measured distance $2.97 \text{ \AA}$., *i.e.*, $d = 5.94 \text{ \AA}$.
- (b) The unit distances along the axes perpendicular to the principal axis are $a = b = c = 8.66 \text{ \AA}$.
- (c) The cell defined by these axes
 - (i.) has volume $3.9 \times 10^{-22} \text{ c.c.}$;
 - (ii.) has mass 6.7×10^{-22} grams;
 - (iii.) contains two molecules and $2 \times 15 = 30$ atoms.

Part III.—ARRANGEMENT OF ATOMS IN THE MINIMUM ELEMENTARY CELL.

10. The arguments, by means of which a position is allotted to each of the thirty atoms of the minimum elementary cell, are now put forward in the order given in the introduction.

Diffraction from Planes normal to the Principal Axis.

11. Diffractions from the (0001) plane are given in Table II. The outstanding features are: (i.) the diffraction corresponding with $2.97 \text{ \AA}$.; (ii.) the strong diffraction corresponding with $1.48 \text{ \AA}$.; and (iii.) the absence of diffractions elsewhere, notably of diffractions corresponding with $5.94 \text{ \AA}$.

The elementary crystal cell is divided, therefore, into four layers $1.48 \text{ \AA}$. apart; these layers will be referred to as planes I., II., III., and IV. respectively.

The diffractions show, further, that whatever may be the distribution of the atoms on each layer, planes

I. and III. are of equal weight, planes II. and IV. are of equal weight, but planes I. and III. differ in weight from planes II. and IV.

*Diffraction from Planes parallel to the Principal Axis.
The Hexagonal Prisms.*

12. Diffractions from the planes $(10\bar{1}0)$ & $(1\bar{2}10)$ are also given in Table II.

For a given wave-length, measurements with the X-ray spectrometer tend to be more intense when the distance between layers is large than when it is small. An intensity of 15 for $1.44 \text{ \AA}$. is therefore considerable in comparison with one of 45 for $4.33 \text{ \AA}$. while an intensity of 35 for $2.52 \text{ \AA}$. is very large when compared with one of 20 for $7.56 \text{ \AA}$. The distances which are of major importance are therefore $2.52 \text{ \AA}$. in planes $(10\bar{1}0)$ etc., and $4.33 \text{ \AA}$. and $1.44 \text{ \AA}$. in planes $(1\bar{2}10)$ etc.

The axial lengths of the crystal in the plane at right angles to the principal axis have been found to be $a=b=c=8.66 \text{ \AA}$. These lengths and the spacings found with the X-ray spectrometer are connected by the relations:

- (i.) Angle between planes $(10\bar{1}0)$ and $(1\bar{2}10)=60^\circ$.
- (ii.) $8.66 \cos 30=7.56=3 \times 2.52$.
- (iii.) $\frac{1}{2} \times 8.66=4.33=3 \times 1.44$.
- (iv.) $4.33=5.77 \sin 60=2 \times 2.89 \sin 60$.

These are the relations given by a regular structure when (i.) its right sections are regular hexagons of side $2.89 \text{ \AA}$., (ii.) the masses are concentrated at the angles of these hexagons, and so lie on straight lines (normal to the hexagons) which form the edges of hexagonal prisms.

These hexagons are shown in diagram 2 (Pl. XIX.) When compared with the cross-section ABCD of the minimum elementary cell, the area of the latter is seen to be three times the area of each hexagon.

The 24 Points of Intersection. Distribution of the Atoms.

13. Each minimum cell contains $2+\frac{1}{2} \times 8=6$ prism edges (see diagram 2, Pl. XIX.). These cut the four layers of atoms normal to the principal axis in $6 \times 4=24$ points of intersection.

The distances between neighbouring intersections are (i.) $1.48 \text{ \AA}$. along the edges of the prisms, *i. e.*, parallel to the principal axis, and (ii.) $2.89 \text{ \AA}$., in the planes normal to these edges.

The value $1.48 \text{ \AA}$. is substantially equal to the value usually found in organic compounds for the diameter of the nitrogen atom. Atoms placed at these points of intersection would be in contact, therefore, with atoms placed at corresponding points of intersection either above or below them, and so would form chains parallel to the principal axis. These chains, however, are separated from one another by $2.89 \text{ \AA}$., *i. e.*, by nearly twice the distance usually found between neighbouring atoms, and are thus too far apart to be held in position by their mutual attractions.

How many atoms lie on the intersections and how are the remaining atoms arranged so as to (i.) hold the chains in a rigid structure and, (ii.) determine the distance $2.89 \text{ \AA}$.? The high symmetry of the crystal enables this question to be answered uniquely.

If all the 24 intersections are occupied by atoms, there remain only $30 - 24 = 6$ atoms to be distributed so as to hold the chains rigidly together.

If, on the other hand, any one section is empty, it follows, from the symmetry of the crystal, that five other intersections similarly situated are also empty. In this case, 18 of the 30 atoms are in the chains, and $30 - 18 = 12$ atoms link the chains together.

A third distribution consistent with the symmetries is 12 atoms in the chains and 18 in the linkages. No other distributions consistent with the symmetry are possible.

When comparing these alternative distributions, it is to be remembered that a high concentration of atoms has been found on the edges of the hexagonal prisms (section 12); if only 12 of every 30 atoms were so situated, this feature of the structure would not predominate in the X-ray diffractions in the way it has been found to do. Against this distribution, it may also be argued that 12 atoms per chain per cell is only two atoms per $5.76 \text{ \AA}$ length of chain; the distance between atoms on a chain would therefore be too great for the (0001) layers to be held together by the chains.

Against the first distribution, 24 and 6, it may be argued on similar lines, that six atoms per cell symmetrically

placed would be insufficient to hold the chains together in a rigid structure.

The second distribution, however, 18 in the chains and 12 in the linkages, is free from such objections, and is accepted as the only possible one. In the argument that follows, it is shown to lead to a structure consistent with the measurements.

Dimensions of the Cyanuric Ring.

14. The above arguments lead to the allotment of 12 atoms per cell for holding together the nitrogen chains in such a way that (i.) the symmetries of the crystal are satisfied, (ii.) the chains are held together rigidly, and (iii.) some explanation is supplied for the spacing of the chains at the apparently arbitrary distance 2.89 Å.

The first of these conditions is satisfied by either an arrangement of six pairs of atoms or an arrangement of two sextets of atoms. The following considerations of the size of the cyanuric ring lead to the choice of the sextet arrangement, and indicate how the second and third conditions may be fulfilled.

The chemical argument for a sextet ring in benzene and its derivatives is similar step by step to that for a sextet ring in cyanuric acid and its derivatives, the one beginning with the polymerization of acetylene, the other with the polymerization of cyanic acid. Does this resemblance persist in the crystal, and can the dimensions of the cyanuric ring be deduced?

Were the cyanuric ring to be constructed on the same lines as the benzene ring found by Lonsdale* in hexamethyl-benzene, it would consist of three nitrogen atoms, arranged alternately, so as to form a regular hexagonal ring in one plane.

The length of side of the hexagon formed by joining the centres of neighbouring atoms would be given by

$$\text{C—N}, \quad \frac{1}{2} \times 1.42 + \frac{1}{2} \times 1.46 = 1.44 \text{ Å.},$$

rather than by

$$\text{C—C}, \quad \frac{1}{2} \times 1.42 + \frac{1}{4} \times 2.142 = 1.42 \text{ Å.},$$

as in the case of benzene. The distance between the centres of atoms at opposite ends of a diagonal PT (see

* Lonsdale, Proc. Roy. Soc. A, cxxiii. p. 494 (1929).

diagram 2, Pl. XIX.) is consequently $2.88 \text{ \AA}$. Since the diameter OQ of the cyanuric ring is greater than this by the sum of the radii of atoms situated at opposite ends of a diagonal, it has, therefore, the value $2.88 + 1.44 = 4.32 \text{ \AA}$.

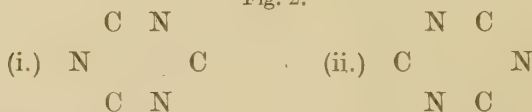
Each elementary prism is defined by six nitrogen chains, and the side of the hexagonal cross-section of each prism is $2.89 \text{ \AA}$.; the diagonal distance HK is consequently $5.78 \text{ \AA}$. The diameter, OQ, of the free space within each prism is less than this by the sum of the radii of atoms situated at its opposite ends; it has therefore the value $5.78 - 1.46 = 4.32 \text{ \AA}$.

A plane cyanuric ring, therefore, formed on the same pattern as the ring in hexa-methyl-benzene, just fits into the space between the nitrogen chains in the crystal of cyanuric triazide, and fulfils the three conditions detailed in the first paragraph of this section.

Situation of the Cyanuric Rings.

15. The diffractions from the plane (0001), see section 11, show that the four atom layers per cell, I., II., III., and IV.,

Fig. 2.



are such that, as regards weight, I.=III. and II.=IV. Taking the plane containing the first cyanuric sextet as plane I. it follows, therefore, that the remaining cyanuric sextet lies in plane III. The fundamental length along the principal axis is, however, $5.97 \text{ \AA}$. (section 9), *i. e.*, twice the distance between the layers I. and III.; the sextets, therefore, while of equal weight, are differently situated in the two planes. This accords with our knowledge of the cyanuric ring, which presents to the nitrogen chains two different aspects depending upon its orientation, see fig. 2. Placing a cyanuric sextet oriented as in (i.) in any particular prism, on plane I., say prism L in diagram 2 (Pl. XIX.), a cyanuric sextet oriented as in (ii.) is therefore placed on plane III.

This cyanuric sextet may be placed on plane III., either in the same prism as the sextet on plane I., *i. e.*, prism L, or in one of the remaining prisms M or N. Some interesting possibilities follow the placing of it in prism L

(see appendix); these, however, are not consistent with the formation of a rigid crystal. On the other hand, by placing it in either of the empty prisms, say prism M, a structure is derived which accords with the crystal now under examination.

Before detailing this structure (section 17), however, the distribution of the nitrogen atoms in the nitrogen chains will be considered.

Arrangement of Atoms on the Nitrogen Chains.

16. There are 18 atoms distributed between 24 points of intersection in accord with the symmetry of the crystal. Each chain therefore contains $18/6=3$ atoms per cell (*i. e.*, per $5.94 \text{ \AA}$. length). These three atoms are distributed among the $24/6=4$ points of intersection per cell on the chain. One point of intersection per chain per cell, therefore, is not filled. Whichever point is unfilled the corresponding points of other cells are also unfilled. The nitrogen atoms, therefore, occur in groups of three along the prism edges, forming short chains separated by spaces corresponding with the unfilled intersections.

The distribution of the unfilled intersections, in accordance with both (i.) the symmetry about the principal axis and (ii.) the equal weight of alternate planes normal to the principal axis, is found possible in one and only one way, *viz.*, calling the planes I., II., III., and IV., and the prism edges 1, 2, 3, 4, 5 and 6 respectively, the unfilled intersections on 1, 3, and 5 lie in one plane and the unfilled intersections on 2, 4, and 6 lie in the next plane of equal weight.

It remains to be determined whether these unfilled intersections occur in the planes I. and III. or the planes II. and IV. If unfilled intersections and the cyanuric sextet both lie in the same plane, the relative weights of consecutive planes will be 6, 9, 6, 9, and the X-ray diffraction corresponding with $1.48 \text{ \AA}$. will be large. If, however, unfilled intersections were to lie in one pair of planes and cyanuric sextets in the other, the relative weights of the planes would be 12, 3, 12, 3, and the X-ray diffraction corresponding with $1.48 \text{ \AA}$. would be weaker than that corresponding with $2.97 \text{ \AA}$. As the X-ray diffraction corresponding with $1.48 \text{ \AA}$ is found to be nine times the greater (Table II.), the former distribution

is the correct one. Cyanuric sextets and unfilled inter-sections, therefore, lie in the same planes.

Part IV.—STRUCTURE AND SOLID CHEMISTRY OF THE CRYSTAL.

Structure of the Crystal.

17. It has been shown in Part III. that (i.) 18 of the 30 atoms of the minimum elementary cell are grouped in straight chains lying on the edges of hexagonal prisms, and (ii.) the remaining 12 may be grouped in sextets; both (iii.) the position of the sextets in the hexagonal prisms formed by the chains, and (iv.) the position of certain empty spaces on the chains have been deduced.

Sufficient data have thus been obtained for the construction of a crystal model on the lines shown in the diagrams (Pl. XIX.) and in the photographs (Pl. XX.).

The diagrams show planes normal to the principal axis. There are four planes per unit elementary cell, equally spaced at a distance apart of $1.48\text{\AA}$. The cross-section, ABCD, of an elementary cell is shown in each diagram.

Alternate planes, the planes II. and IV., are shown in diagram 5 (Pl. XIX.). These consist of nitrogen atoms at each of the intersections of the prism edges (compare diagram 2) with these planes.

Plane I. is shown in diagram 3 (Pl. XIX.). It contains the atoms of the sextet oriented as in fig. 2 (i.) and situated in the hexagonal prism L. The intersections with the prism edges are alternately unfilled and filled with a nitrogen atom.

Plane III. is shown in diagram 4 (Pl. XIX.). It contains the atoms of the sextet oriented as in fig. 2 (ii.) and situated in the hexagonal prism M. The intersections with the prism edges are alternately unfilled and filled with a nitrogen atom.

Further planes may be obtained by repetition of I., II., III., and IV.

Diagram 6 (Pl. XIX.) is formed by the superposition of diagrams 4 and 5 (Pl. XIX.).

In the models, the small cubes indicate the position of the centres of the atoms.

Photograph I. (Pl. XX.) shows a model rotating about

the principal axis. The atoms are seen to lie in equally spaced planes.

In photographs II., III., and IV. (Pl. XX.) the small model on the left represents a unit elementary cell (corresponding with ABCD in the diagrams (Pl. XIX.)). The large model in the centre represents a portion of the crystal equal in volume to six such elementary cells; its centre corresponds with the point B on the diagrams. The model on the right represents a block of 15 atoms corresponding with the 15 atoms of the chemical molecule.

TABLE III.
Relative Intensity of X-ray Diffractions.

	From measurements.	Calcd. from model.
Plane (0001):		
Spacings	2.97 Å., 1.48 Å.	5.94 Å., 2.97 Å., 1.48 Å.
Approx. ratio of intensities ..	0.11 : 1.0	0.0 : 0.15 : 1.0
Plane (1 $\bar{2}$ 10):		
Spacings	4.33 Å., 2.17 Å., 1.44 Å.	8.66 Å., 4.33 Å., 2.88 Å., 2.17 Å., 1.44 Å.
Approx. ratio of intensities ..	1.0 : 0.6 : 0.3	0.0 : 1.0 : 0.0 : 0.7 : 0.3.
Plane (10 $\bar{1}$ 0):		
Spacings	7.56 Å., 2.52 Å., 1.26 Å.	7.56 Å., 3.78 Å., 2.52 Å., 1.89 Å., 1.26 Å.
Approx. ratio of intensities ..	0.6 (?) : 1 : 0.6	0.8 : 0.0 : 1.0 : 0.0 : 0.8
Plane (1 $\bar{2}$ 11):		
Spacing	4.92 Å.	4.92 Å.
Plane (10 $\bar{1}$ 1):		
Spacing	4.70 Å.	4.70 Å.

In photograph II. (Pl. XX.) the models are viewed along the principal axis. The nitrogen chains are foreshortened, and the hexagonal prisms are seen either (i.) empty as at A, B, C, and D in the diagrams (Pl. XIX.), or (ii.) containing sextets as at L and M.

In photographs III. and IV. (Pl. XX.) the models are viewed normal to the principal axis at such angles that the (1210) planes and the (1010) planes respectively are foreshortened. The spacings thus shown may be compared with the diffractions given in Table II.

In Table III. the spacings calculated from the measured X-ray diffractions and the relative intensities of the latter

are compared with those calculated* from the model. Agreement is shown within the limits of accuracy of the calculation and of the measurements.

In Table IV. some further properties deduced from the model are compared with the observed properties.

TABLE IV.
Some Properties of Cyanuric Triazide.

	Observed.	Deduced from model.
Crystal shape ..	Hexagonal holohedral.	Hexagonal holohedral.
Axial ratio	0.684	0.684
Prism - pyramid angle.	51° 41' 45"	51° 45'
Miller's element .	38° 18' 15"	38° 15'
Optical activity.	Neutral.	Neutral.
Etched figures ..	Straight lines parallel principal axis.	Straight lines parallel principal axis, determined by empty prism (see photograph 2).
Planes of cleavage.	Absent.	Absent.
Density	1.71	1.71 ₅

The Solid Chemistry of the Crystal.

18. The model is found to consist of groups of 15 atoms corresponding with the 15 atoms of the chemical molecule. The minimum distance between the centre of an atom of one such group and the centre of the nearest atom of a neighbouring group is rather more than 2.0 Å., whereas the maximum distance between the centres of neighbouring atoms in the same group is 1.48 Å. The molecules of cyanuric azide, therefore, form distinct separate entities within the crystal as is typical of organic molecules. There is no evidence of polymerization or of dissociation.

The azide grouping is found to consist of three nitrogen atoms arranged in a short chain set at right angles to the plane of the cyanuric ring, and attached to it by means of

* See Wyckoff, 'Structure of Crystals,' p. 107 (20).

the middle nitrogen. This structure is similar to that given by Hendricks and Pauling* for the azide group in alkaline azides, and contrasts sharply with the ring structure indicated by the dipole moments of a number of liquid organic azides. The evidence for both these structures has been discussed by L. E. Sutton† and T. C. Sutton‡.

The effective diameter of the nitrogen atom in the azide chain is $1.48^{\circ}\text{\AA}$., while in the cyanuric ring on which the model is based it is $1.46\text{\AA}$. Ring nitrogen and chain nitrogen, therefore, have not shown differences corresponding with those shown by ring carbon and chain carbon, *i. e.*, $1.42\text{\AA}$. and $1.55\text{\AA}$. respectively.

In estimating the dimensions of the cyanuric group (section 14), use has been made of its resemblance to the benzene ring. The way in which arguments based on this resemblance have led to a logical and consistent explanation of the measured properties of the crystal, gives further support to the view that the cyanuric group, like the benzene group, is a ring of six atoms so arranged that (the spheres of influence of) neighbouring atoms are in contact, *i. e.*, their centres are $1.44\text{\AA}$. apart.

Among the friends to whose interest and assistance the author is indebted, he would particularly mention his chief, Dr. Godfrey Rotter, who has made the research practicable, Professor A. W. Porter, who permitted the X-ray measurements to be made in his laboratory, Dr. H. H. Thomas, and Sir Robert Robertson.

APPENDIX.

Linear Crystals.

In section 15 reference has been made to the structure obtained by placing the two cyanuric sextets in the same hexagonal prism L, instead of in two neighbouring prisms, L and M. Whereas the latter leads to the formation of hexagonal crystals such as have been found in practice, the former leads to a highly speculative structure which from its tenuous nature may be difficult to isolate or to detect.

The structure consists of hexagonal prisms (such as L) in which alternate layers contain a cyanuric sextet. It

* Hendricks and Pauling, J. A. C. S. xlvii. p. 2904 (1925).

† L. E. Sutton, 'Nature,' Oct. 9, 1931, p. 693.

‡ T. C. Sutton, 'Nature,' Nov. 21, 1931, p. 872.

may be obtained from the molecules by placing one molecule (see iii. in photographs) directly above another similar molecule in such a way that the lower ends of the azide chains of one molecule fit into the spaces between the upper ends of the azide chains of the other molecule, and repeating the process indefinitely.

Such a structure would appear to be stable and capable of growth lengthwise to an indefinite extent. All the sextets, however, lie within the one hexagonal prism formed by the azide chains and no atoms are available to link the prism to other prisms. Conditions are, therefore, unfavourable to lateral growth.

LXXX. *Atomic Moments in Ferromagnetic Metals and Alloys with Non-Ferromagnetic Elements.* By EDMUND C. STONER, Ph.D. (Cambridge), Reader in Physics, University of Leeds*.

ALTHOUGH an unforced theoretical interpretation can now be given of the general characteristics of ferromagnetic phenomena, there is no completely satisfactory interpretation of the actual values found for the magnetic moments per atom in ferromagnetic metals and alloys. By extrapolation from the values observed for the magnetization in high fields at a series of low temperatures the saturation magnetization at absolute zero may be deduced with but little uncertainty; this value corresponds to parallel alignment of the carriers, so that the magnetic moment per atom is obtained simply by dividing by the number of atoms. The values found for nickel and iron are 3.0 and 11.0 Weiss magnetons (μ_W), the Weiss unit being in fact the highest common factor of the moments of the iron and nickel atoms found in this way. For cobalt the value is about 8.6. Now the gyromagnetic ratio for ferromagnetics (at room temperature) is within a few per cent. of 2, so that at least at low temperatures, the moment may be regarded as almost entirely due to electron spin. If an integral number of effective electron spins are contributed by each atom it would therefore be expected that the moments observed would correspond to integral numbers

* Communicated by Prof. R. Whiddington, F.R.S.

of Bohr units (μ_B) or integral multiples of approximately $5\mu_W$ (more accurately of $4.943\mu_W$). If the carriers themselves have integral moments (in Bohr units, with zero moment as one possibility) the observed values can, of course, be accounted for by assuming the ferromagnetic to contain a mixture, in appropriate proportions, of neutral atoms and ions, or atoms or ions in different quantum states. The objections to the particular suggestions which have been made will be mentioned later.

It has long been known that when non-ferromagnetic elements are added to ferromagnetics to form alloys there is, in general, a decrease in the magnetic moment per atom and also of the Curie temperature. When copper is added to nickel, for example, there is a linear decrease in the moment from $3\mu_W$ to 0 at approximately 60 per cent. Cu. At the same time the Curie point decreases linearly towards absolute zero. A linear change over so wide a range of concentration is exceptional, but with many elements there is an approximately linear variation of moment with concentration at low concentrations. The effective moment per added atom of the foreign element may then be found from the initial part of the concentration, magnetic moment curve. Thus in the case of Ni-Cu the extrapolated value for 100 per cent. Cu is -2.09 . (In general it is the tangent to the initial part of the curve which must be extrapolated.) In a recent comprehensive investigation Sadron⁽¹⁾ has made measurements on a large number of alloys from this point of view, and has arrived at a series of "ferromagnetic moments" of non-ferromagnetic elements. Thus to copper atoms added to nickel a moment of $2.09\mu_W$ is attributed, and the moments are supposed to set themselves anti-parallel to the nickel moments of $3.0\mu_W$ per atom. Some striking periodic regularities are found in the moments so deduced for different elements; but unless the reality of the Weiss magneton is accepted, for which there seems now no justification, in spite of the possible utility of the unit in expressing experimental results, no theoretical significance can be attached to the values given. It is the main purpose of this paper to put forward an interpretation of some of the salient features of the results which is consistent with well established theory.

THE EXPERIMENTAL RESULTS.

The experimental results to be considered here are those for the atomic moments in ferromagnetic metals and in some of the binary alloys as obtained from measurements of the saturation magnetization at low temperatures. The moments are derived in a direct manner from the empirical results, and the effects of temperature need not be considered. Moreover, the fact that the experimentally determined gyromagnetic ratio is close to 2 at room temperature for Fe, Cu, and Ni, and also Heusler alloys enables the treatment to be simplified, for it is only electron spin which contributes appreciably to the magnetic moment. It is mainly nickel alloys which will be considered, because more extensive data are available for them than for those of other ferromagnetic metals, and because the characteristics to be discussed are here less likely to be obscured by complicating factors.

Accurate measurements of the magnetization of ferromagnetics at low temperature have been made by Weiss and Forrer⁽²⁾. The following values are obtained for the atomic moments, expressed in terms of the Weiss magneton (1125.6 per gm. mol.), for the ferromagnetic elements:—

TABLE I.

Atomic Moments of Fe, Co, Ni (μ_w).

Fe.	Co.	Ni.
11.0	8.6	3.0

The saturation magnetization of a large number of alloys has been measured by Sadron⁽¹⁾. The "ferromagnetic moment" of the foreign element is obtained by extrapolation of the initial linear part of the atomic moment, atomic concentration curve to 100 per cent. of the foreign element, as explained above. The values obtained for alloys with nickel are shown in the following table. The moment of nickel being 3, a value algebraically less than +3 indicates that addition of the foreign element results in a decrease of moment. None of the non-ferromagnetic foreign elements added gave an increase of moment except Mn. The atomic number of the element is given and also its column in the simple form of the periodic table.

TABLE II. *a.*

Ferromagnetic Moments of Elements in Nickel for small concentrations in Nickel. (Weiss magneton units, μ_W .)

1.....	Cu (29) — 2.09	6.....	Cr (24) — 19.0
2.....	Zn (30) — 7.3		Mo (42) — 19.5
3.....	Al (13) — 12.2		W (74) — 19
4.....	Sn (50) — 18.0	7.....	Mn (25) + 15.1
5.....	V (23) — 22.96	8 i.	Ru (44) — 10.8
	Sb (51) — 24.4	iii.	Pd (46) + 3.0

The precision of the above values varies considerably. The range of approximately linear variation is less than 10 per cent. except for Cu (57 per cent.), Zn (16 per cent.), and Ru (12 per cent.), and comparatively small errors in the measurements (or in the analysis of the alloys) may have a large effect on the extrapolated values. (Sadron's paper should be consulted in this connexion and also for the detailed results as to variation of moment at higher concentrations.)

For completeness the results for alloys with Co may be quoted

 TABLE II. *b.*

Ferromagnetic Moments in Cobalt (μ_W).

1.....	Au (79) + 2.3	7	Mn (25) — 15
2.....	Si (14) — 17.8	8 iii.	Pt (78) + 2.9

It may be noted that the result for Au is very uncertain, though the values for the other elements should be comparable in precision with those in the previous table. A very rough extrapolated value of +1 is obtained for Mn in Fe.

PREVIOUS INTERPRETATIONS.

Ferromagnetic Elements.

To account for the fact that the atomic moments of ferromagnetic elements are not integral multiples of the Bohr unit ($\mu_B = 4.943\mu_W$) it was suggested by Stoner⁽³⁾ (1926) that a ferromagnetic should be regarded as an

equilibrium mixture of neutral atoms, ions, and free electrons, the electrons making no contribution to the resultant moment, and the atoms and ions a contribution corresponding to their spin moments in their normal state. By making appropriate assumptions as to the relative numbers of atoms and ions present it was then possible to account more or less quantitatively for the observed moments at low temperatures, and for the moments deduced from the variation of the paramagnetic susceptibility above the Curie point. To this there is the objection that there would be differences in the lattice-point systems, some being neutral atoms, others ions in different stages of ionization, and that the particular type of equilibrium required was of a kind for which no satisfactory basis could be given. It is now clear, moreover, that too sharp a distinction was made between "free" electrons and electrons in atoms or ions in the metal.

It has been suggested by Wolf⁽⁴⁾ (1931) that the facts can be explained by assuming that the metal consists of a mixture of neutral atoms in states corresponding to different possible spectroscopic states for the free atoms; in nickel, for example, of a mixture of ^3F and ^1D states, with spin moments of 2 and $0\mu_B$, in the proportion 3 to 7. He advances arguments to show that such a mixture could give rise to a stable equilibrium. Even for nickel, however, the wave number difference between the ^3F and lowest ^1D state is 3410, corresponding to a temperature (putting $kT = h\Delta\nu$) of about 3000° ; and it is difficult to see why some 70 per cent. of the atoms should be in the higher energy state at low temperatures.

Alloys.

In Sadron's discussion^{(1) (5)} the experimental results are taken at their face value, as giving direct indications of the magnetic moments of the atoms present, in much the same way as in Forrer's⁽⁶⁾ treatment of binary alloys of ferromagnetic metals. (The reality of the Weiss magneton is virtually accepted, and different magneton values for the same element are taken as indicating that the atoms may occur in different magnetic states.) It is assumed that the moments of the substituted solute atoms may set themselves either parallel or antiparallel to the

moments of the atoms of the ferromagnetic solvent; so that the moments are taken to have the numerical values given in Table II., a negative sign there simply indicating antiparallel setting. From this restatement of the experimental results certain regularities emerge. It will be seen from Table II. *a* that there is a rise and fall in the atomic moments in proceeding across the periodic table, elements in the same column having approximately the same moment. The numerical values found from Co alloys (Table II. *b*) agree roughly with those from Ni alloys for elements in the same column; but the agreement is hardly sufficiently extensive for much stress to be laid on it, particularly as Mn in Fe gives a completely different value from that in Ni and Co. There is undoubtedly significance in the regularities which are brought out, but the treatment as a whole seems rather to "beg the question."

Dorfman ⁽⁷⁾ has suggested an interpretation of some of the regularities on the basis of the view discussed above that a ferromagnetic consists of a mixture of atoms and ions, with free electrons not contributing to the ferromagnetism. He supposes that nickel consists of a mixture of 40 per cent. neutral atoms with zero moment and 60 per cent. of Ni ions with a moment of $1\mu_B$; further, that foreign atoms entering the Ni lattice become singly ionized. The results are then in fair agreement with the values 0, -1, -2, and -3 for singly ionized Cu, Zn, Al, and Sn. This view is open to the objections previously mentioned, and there is the additional arbitrary feature in that the foreign atoms are supposed to be uniformly in a singly ionized state. But here again a regularity which is undoubtedly significant has been noted.

SUGGESTED INTERPRETATION OF ATOMIC MOMENTS.

(i.) *Ferromagnetic Elements.*

(a) *General.*—That the "carriers" of the magnetic moment in ferromagnetics are electron spins is shown by the value of gyromagnetic ratio; confirmatory evidence is provided by the form of the magnetization, temperature curves below the Curie point ⁽⁸⁾. The individual carriers then have a moment of $1\mu_B$, and can set themselves parallel or antiparallel to the direction of magnetization. The

essential fact which has to be explained is that the magnetic moment per atom in the ferromagnetic elements is not an integral number of Bohr units. From Table I. the values are

Fe.	Co.	Ni.
2.22	1.7	0.606 μ_B

It must be borne in mind that crystal analysis gives no grounds for the assumption of differences in the states of the atoms in a typical metal. It is therefore reasonable to attempt to derive the states of a crystal from those of an aggregate of the free neutral atoms in their normal states brought into interaction with each other.

The case of Ni will be considered. The normal state of the atom is $3F d^8 s^2$. Apart from the completed group of eighteen electrons there are, as far as spin is concerned, three balanced pairs of d electrons, one balanced pair of s electrons, and two unbalanced (parallel) d electrons. (Of the $5 \times 2 d$ states 3×2 are occupied by electrons in balanced pairs and 2×1 by unbalanced electrons.) Now in the case of atoms with one loosely bound electron outside a completed core (*e. g.*, sodium) the effect of interaction is that the electrons fill an energy band which, for loose binding, approximates to that for the so-called free electrons. When the binding force (or the variation in potential with position) is small the distribution is obtained by a simple application of the Fermi-Dirac statistics. At absolute zero (and approximately up to high temperatures) the pairs of cells corresponding to the lowest momentum (and lowest kinetic energy) are occupied by pairs of electrons with oppositely directed spins. The substance has no resultant magnetic moment, but, as shown by Pauli⁽⁹⁾, will have a small paramagnetism varying only slightly with temperature. The numerical results obtained by this treatment are in reasonable agreement with the values found for the alkali metals. The effect of stronger binding (or larger variation of potential with position) is that the energy band is narrowed. For n atoms each band can accommodate $2n$ electrons. If the question is approached from the other end, taking the energy levels of the separated atoms as the first approximation, the effect of interaction is to widen these levels into bands, the width increasing with

the interaction. This very brief outline is probably sufficient for the present purpose to indicate the general character of the treatment of the theory of metals developed by Bloch, Peierls, Brillouin, Wilson, and others⁽¹⁰⁾, whose papers should be consulted for fuller details. In ferromagnetics it is essential, as shown by Heisenberg⁽¹¹⁾, that the interaction integral should be positive, of opposite sign to that for two hydrogen atoms. The state of lowest energy is then that in which the electron spins are parallel. To revert to the case of Ni, the ferromagnetic interaction occurs between the unbalanced d electrons in the different atoms. The cells in the energy band occupied by these electrons in the metal may be regarded as derived from the aggregate of cells contributed by the atoms at the rate of four per atom. With normal interaction the state of lowest energy would correspond to the filling of the lowest cells, in pairs, by pairs of electrons with antiparallel spins. The tendency to this state, however, is opposed by the tendency towards parallel setting of the electrons, this corresponding to a lower potential energy owing to the interaction integral being positive. For nickel the equilibrium state corresponds to an excess of .6 unbalanced electrons per atom.

(b) *Formal treatment.*—A formal expression for the dependence of the energy on the atomic moment may readily be written down. Let n be the number of atoms per unit volume, q the number of unpaired electrons per atom in the free atom, x the number of parallel spins per atom in the metal, so that the atomic moment is $x\mu_B$. Then the part of the energy $E(nx)$ dependent on x is

$$E(nx) = f_0 \left\{ \frac{n(q+x)}{2} \right\} + f_0 \left\{ \frac{n(q-x)}{2} \right\} - f_1(nx).$$

The equilibrium state considered is illustrated by the diagram (which corresponds to the case of nickel).

The equilibrium state occurs for

$$\frac{dE(nx)}{d(nx)} = 0.$$

In the diagram the kinetic energy may be regarded as increasing upwards. The equilibrium corresponds to equality of total energy of the electrons in the cells of highest kinetic energy in the two groups $n(q+x)/2$

and $n(q-x)/2$ of parallel electrons, the excess of unpaired electrons having a lower potential energy owing to the interaction.

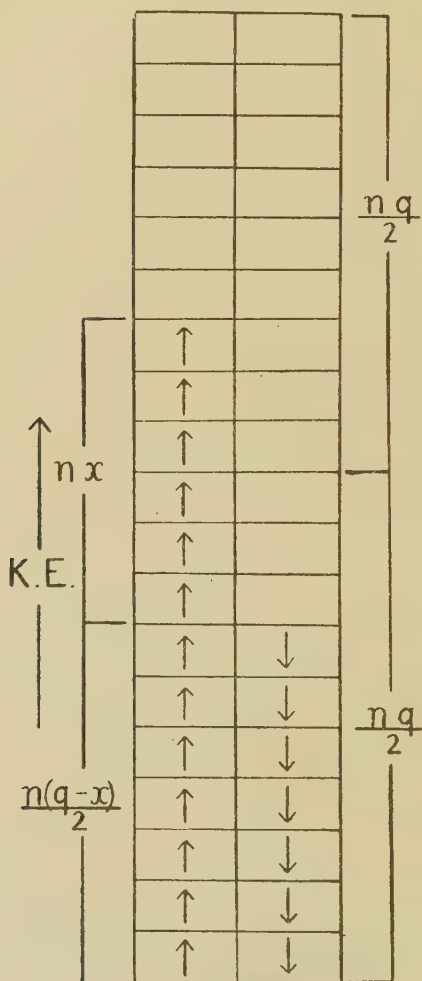


Diagram representing equilibrium state for $n=10$, $q=2$, $x=0.6$.

The term $f_J(nx)$ is the interaction energy term (corresponding to $\frac{1}{2}NI^2$ in the Weiss theory). As an approximation

$$f_J(nx) = \frac{zJ_0}{4n}(nx)^2,$$

where J_0 is the interaction energy ($2J_0$ being the difference in the energy of a pair of electrons in the parallel and antiparallel states), and z the number of effective neighbours for interaction. (This corresponds to the expression $(zJ_0/n)S'^2$ given, for example, by Van Vleck ⁽¹²⁾, where S' is the total spin moment of the volume considered.) In the original form of Heisenberg's theory it was supposed that only interaction between neighbouring atoms need be taken into account, so that z represented the number of nearest neighbours of each atom (twelve for Ni, eight for Fe). Later work ⁽¹³⁾, however, indicates that J_0 may be an increasing function of interatomic distance for values actually concerned. With increase of distance between a pair of atoms J_0 at first increases and then decreases with distance r , being appreciable up to distances of, say, r_1 . The expression zJ_0 should then be replaced by

$$\int_0^{r_1} 4\pi r^2 n \left(J_0 + \frac{dJ_0}{dr} \right) dr.$$

If only nearest neighbours within a distance r_0 are to be considered, this reduces to

$$\frac{4\pi}{3} r_0^3 n J_0 = zJ_0.$$

In general, however, zJ_0 may approximately be replaced by

$$\alpha n \bar{J}_0,$$

where, as an approximation,

$$\alpha n \bar{J}_0 = zJ_0.$$

With the more general expression the interaction energy becomes

$$f_J(nx) = \frac{\alpha J_0}{4} (nx)^2,$$

and is simply proportional to the square of the intensity of magnetization.

It is not possible at present to give a precise and general expression for $f_0(nq)$. For free electrons, without interaction,

$$f_0\left(\frac{nq}{2}\right) = f_0(y) = \frac{3\hbar^2}{40m} \left(\frac{6}{\pi}\right)^{2/3} y^{5/3}.$$

For $x=0$ the expression for the total energy becomes

$$E = \frac{3}{40} \frac{\hbar^2}{m} \left(\frac{3}{\pi} \right)^{2/3} (nq)^{5/3} = E_0(nq),$$

the usual expression for the zero point energy per unit volume of a free electron gas having nq electrons per unit volume. The effect of a periodic perturbing potential (such as arises from the fields of the atoms at the lattice points) is that the continuous range of energy possible for free electrons is split up into a series of bands of allowed energies, each band being capable of accommodating $2n$ electrons. Explicit solutions of the equations have been obtained only for idealized cases, but the general effect is clear. The width of the bands decreases with the strength of the atomic fields; conversely the energy levels of bound electrons in incomplete groups in free atoms widen into bands in an aggregate, and their width increases with the strength of interaction. Thus the normal width of the energy band corresponding to the d electrons in ferromagnetic metals (represented by the height for $nq/2$ electrons in the diagram) will be much less than the width for the same number of "free" electrons. Let E_d represent the width of the band due to the unpaired d electrons without the ferromagnetic interaction. Then

$$E_d(nq) = \gamma E_0(nq), \quad \gamma < 1,$$

where E_0 is the width for free electrons. The functional dependence of E_d on nq will differ from that of E_0 , and no further exact calculations can be made until more is known about this functional dependence. Certain points are, however, brought out by the purely provisional assumption that the dependence is of a similar kind to that for free electrons. The equation for the energy may then be written

$$E(nx) = 2^{2/3} \gamma \left\{ E_0 \left(\frac{nq + nx}{2} \right) + E_0 \left(\frac{nq - nx}{2} \right) \right\} - \frac{\alpha J_0}{4} (nx)^2.$$

It is from an equation of this type that nx may be determined by differentiation. The two terms in this equation are approximately proportional to γT_0 and to θ , where T_0 is the temperature corresponding to the zero point energy

of free electrons (of the order 10^4) and θ is the Curie temperature (of the order 10^3). Straightforward consideration of the equation shows that ferromagnetism will only occur (*i. e.*, energy a minimum for $x > 0$) for

$$\gamma T_0 < 0 \frac{q}{x} \theta.$$

A relation of this kind will hold even if the functional dependence of E_d on nq differs from that provisionally assumed, for γT_0 is proportional to the width of the band without the ferromagnetic interaction and θ to the part corresponding to the unpaired electrons (see diagram). Were $E_d(nq)$ known, and also J_0 , it should be

TABLE III.
Data for Ferromagnetic Metals.

Element.	Fe.	Co.	Ni.
Normal state of atom	$5D(d^6s^2)$	$4F(d^7s^2)$	$3D(d^8s^2)$
Number of parallel spins in atom. q	4	3	2
Number of parallel spins per atom in metal. x	2.2	1.7	0.6
x/q	.55	.57	.3
θ ° Abs.	1043	1404	630

possible, knowing q , to calculate x and θ (*i. e.*, the atomic moment and the Curie temperature). For the present, however, it is necessary to take x as experimentally determined, and from it to derive information about $E_d(nq)$, just as an estimate of J_0 may be made from θ . It is hoped that further progress may be made along these lines. It may be noted that there is an indication of decreasing energy band width in the elements preceding the ferromagnetics in the increasing paramagnetic susceptibility of the elements Ti, V, Cr, and Mn (Peierls⁽¹⁰⁾). The purpose at present, however, is to apply the general idea to a consideration of moments in the simpler ferromagnetic alloys, for which the matters of quantitative detail are of less importance. In Table III. the values of

x and q for the ferromagnetic metals are given, and also the Curie temperatures.

Although the above treatment is almost inevitably qualitative it does seem to provide an approach to the problem of atomic moments of ferromagnetics which is consistent both with general spectroscopic theory and with the theory of the metallic state—that is to say, consistent with the body of experimental facts on which those theories rest. It has been presented as simply as possible in order that the main ideas may not be obscured by the many details which would have to be considered in a more complete treatment.

(ii.) *Ferromagnetic Alloys.*

The substitution of δn foreign atoms in place of δn atoms of the ferromagnetic metal may be regarded as occurring in two stages; δn atoms are first removed, and δn foreign atoms are then added. Let Z be the number of electrons in the neutral atom of the ferromagnetic. $Z - q$ of these are in complete groups, and q are unpaired electrons which contribute to the nq collective electrons in the metal. With the removal of $\delta n \times q$ collective electrons the new state of lowest energy will correspond to x' unpaired electrons per atom in the metal, the total number of unpaired electrons being $(n - \delta n)x'$. As long as $\delta n/n$ is small, however, this number will be the same as the original nx , for the state of lowest energy will be obtained by removing equal numbers of electrons in the highest kinetic energy states in the two groups $n(q + x)/2$ and $n(q - x)/2$ (see diagram). If δn foreign atoms are now added, with electrons entirely in firmly bound complete groups, the total number of unpaired collective electrons will remain unchanged—that is, the average magnetic moment per atom will be unchanged. This corresponds to what occurs when Pd is added to Ni (Table II. *a*). When there are loosely bound electrons in incomplete groups in the foreign atoms these will interact with the original collective electrons. As long as the interaction integral is not positive the state of lowest energy will correspond to the antiparallel setting of the spins of the added electrons, and the total moment will be reduced. Thus when Cu is added to nickel the effect of the unpaired s electron in each Cu atom is to reduce the total moment

by $1\mu_B$. In a similar way, under favourable conditions as to the energy relations, there will be a reduction in the total moment of $1\mu_B$ for each loosely bound potentially unpaired electron in the added atoms. That a number of the salient facts is covered even by this idealized scheme is shown by the following table, in which the change in moment per added atom in Bohr units is given for foreign atoms in nickel. The values are derived from those in Table II. *a*, the moment per nickel atom in nickel itself being 0.60μ .

Considering the uncertainties in connexion with the analysis of low concentration alloys, and the various extrapolations which are necessary in deriving the values

TABLE IV.

Decrease in magnetic moment per added foreign atom in nickel alloys. (Bohr units. $\mu_B = 4.943\mu_W$.)

1.....	Cu (29)	1.01	6.....	Cr (24)	4.45
2.....	Zn (30)	2.14		Mo (42)	4.55
3.....	Al (13)	3.07		W (74)	4.45
4.....	Sn (50)	4.25	7	Mn (25)	2.45
5.....	V (23)	5.25	8 i.	Ru (44)	2.79
	Sb (51)	5.52	iii.	Pd (46)	0.0

from the experimental results, the closeness of the agreement of the change in moment with the number of valency electrons is in many cases very striking, for it is only in exceptional circumstances that anything approaching exact agreement (such as occurs for Cu) with the predictions of a very idealized treatment would be expected. It must further be stressed that it is only for very small concentrations of foreign atoms that it is justifiable to assume that the total moment due to the nickel atoms will be unchanged. Bearing this in mind, the particular cases call for but brief discussion.

The number of loosely bound potentially unpaired electrons may be taken as equal to the normal valency in such atoms as Cu, Zn, Al, and possibly Sn—that is, to 1, 2, 3, and 4 respectively. The experimental values for the moments in Sn–Ni alloys are rather scattered, the values for the change of moment per atom being 4.00, 4.35, 4.16,

4.16, and 4.30 for five concentrations up to 5.94 per cent.; the results are thus not incompatible with a value 4.0 for low concentrations. For both vanadium and antimony the values are based on extrapolation of only two experimental values at concentrations of less than 2.5 per cent., and so can hardly be regarded as at all certain. The valency of elements on the right-hand side of the periodic table is in general much less well defined. The normal state of Cr, ^7S , would indicate a potential valency of 6, but there are many compounds corresponding to a smaller valency. For W the ^5D state is the lowest. The observed effects of the elements of the sixth column as foreign atoms in nickel are thus compatible with their chemical and spectroscopic character. A contribution of two unpaired electrons might be expected from Ru, though its normal state is ^5F . The zero effect of Pd is in agreement with its ^1S normal state.

Manganese is unique among non-ferromagnetic elements in producing an increase in moment. It has been pointed out by Slater (¹⁴), however, that the occurrence of positive interaction such as occurs in ferromagnetic metals is associated with a large value of the ratio of the interatomic distance to the sum of the effective radii of the incomplete d shells. As has been discussed elsewhere (¹⁵) this ratio is greater for Mn-Ni than for iron. A positive interaction is therefore in harmony with the known facts as to the interaction integral, and this will be associated with a tendency to parallel rather than antiparallel setting of the added spins. The ratio for Mn-Co or Mn-Fe, however, is smaller than in iron, and manganese correspondingly produces in Co and Fe a decrease in moment. In Co the decrease per atom of added Mn is $23.6\mu_W$ (Table II. *b*), or approximately $4.7\mu_B$ which is compatible with the ^6S state of Mn. For Mn in Fe the decrease is approximately $2\mu_B$. The region of the periodic table concerned is critical in respect of the sign of the interaction integral, and no simple relations would be expected.

The very uncertain value of $2.3\mu_W$ for Au in Co corresponds to a decrease in moment of $6.3\mu_W$ per atom added; and as the extrapolated result may here be in error by more than 50 per cent., this is compatible with a decrease of $1\mu_B$ per atom under idealized conditions. The decrease of moment due to Si in Co, namely, $26.4\mu_W$ per atom, is certainly greater than would be anticipated; but the

Si-Co alloy is of a much more complex character than the other alloys considered. Pt in Co produces a decrease of moment of $5.7\mu_W$ per atom; this may be associated with the fact that the normal state of the Pt atom is ^3D (in contrast to ^1S for Pd, which at low concentrations has no effect in nickel).

From the above brief discussion it appears that the treatment suggested provides a satisfactory interpretation of the general character of the whole of Sadron's results for the variation of moment at low concentrations.

It does not seem possible at present to extend the treatment to yield quantitative predictions in the more complex cases. In simple cases the treatment indicates that there will be a decrease of moment per atom when foreign elements are substituted in ferromagnetic metals (except when the interaction is positive), and that the decrease in moment per substituted atom will be a multiple of the Bohr unit, the multiple being equal to the valency of the foreign atoms—that is, to the number of loosely bound potentially unpaired electrons in them. This is precisely what is found. In more complex cases only rough predictions can be made. Consideration of the individual cases, however, indicates that the apparent irregularities (apart from the experimental uncertainties) are of a kind which is compatible with the general outlook when the various complicating factors are taken into account.

SUMMARY.

A summary is given of the experimental results for the magnetic moment per atom in ferromagnetic metals at low temperatures, and of the results of Sadron for the change in the average atomic moment due to the substitution of foreign elements (Tables I. and II.).

The magnetic moment is due almost entirely to electron spin, but the atomic moments are not in general integral multiples of the Bohr unit. The unsatisfactory features in previous suggested interpretations of the experimental values are pointed out.

The view is put forward that the observed values of the atomic moment in ferromagnetic elements correspond to an equilibrium resulting from the normal tendency to antiparallel setting of the spins of interacting electrons

in a metal (owing to their occupying the lowest momentum ranges in an energy band) being opposed by the tendency to parallel setting, due to the interaction integral being positive. The equilibrium considered is represented in the figure. A formal treatment of the equilibrium is given. It is shown that the ratio of the number of unpaired electrons per atom in the metal (x) to the number in the free atom (q) will be of the same order as the ratio of the "ferromagnetic" interaction energy to the width of the energy band, or of θ to T_0 , where θ is the Curie temperature, and T_0 the temperature corresponding to the band width. Relevant data are given in Table III.

It is shown that in simple cases the substitution of foreign elements will result in a decrease of total moment (except when the interaction is positive), the decrease in moment per substituted atom in Bohr units being equal to the valency of the atom (Table IV.). This holds closely for Cu, Zn, Al, and Sn in Ni. In other cases only rough predictions can be made, but the experimental results as a whole are compatible with the outlook suggested.

References.

- (1) C. Sadron, *Ann de Phys.* xvii. p. 371 (1932).
- (2) P. Weiss and R. Forrer, *Ann. de Phys.* xii. p. 279 (1929).
- (3) E. C. Stoner, *Proc. Leeds Phil. Soc.* i. p. 55 (1926); *Phil. Mag.* x. p. 27 (1930).
- (4) A. Wolf, *Zeits für Phys.* lxx. p. 519 (1931).
- (5) For further discussion, see Congrès International d'Electricité, Paris, (1932). Section 1, Report 14 (L. Néel); Report 15 (P. Weiss).
- (6) R. Forrer, *Journ. de Phys.* i. p. 325 (1930).
- (7) J. Dorfman, 'Nature,' cxxx. p. 506 (1932).
- (8) F. Tyler, *Phil. Mag.* ix. p. 1036 (1930); xi. p. 596 (1931); E. C. Stoner, *Phil. Mag.* xii. p. 737 (1931).
- (9) W. Pauli, *Zeits. für Phys.* xli. p. 81 (1927); see also F. Bloch, *ibid.* liii. p. 216 (1929).
- (10) For a summary of the electron theory of metals see R. Peierls, *Ergeb. der ex. Naturwissenschaften*, xi. p. 264 (1932), or A. H. Wilson, *Proc. Roy. Soc.* cxxxiii. p. 458 (1931).
- (11) W. Heisenberg, *Zeits. für Phys.* xlix. p. 619 (1928).
- (12) J. H. Van Vleck, 'The Theory of Magnetic and Electric Susceptibilities,' Ch. XII. Oxford (1932).
- (13) F. C. Powell, *Proc. Phys. Soc.* xlii. p. 390 (1930).
- (14) J. C. Slater, *Phys. Rev.* xxxvi. p. 57 (1930).
- (15) E. C. Stoner, *Proc. Leeds Phil. Soc.* ii. (1933).

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LXXXI. *The Diffusion of Monatomic Gases through Fused Silica.* By T. ALTY, D.Sc., Ph.D., Research Professor of Physics, University of Saskatchewan, Canada*.

Introduction.

IT has long been known that at high temperatures many of the permanent gases diffuse slowly through fused silica. A number of experimental investigations of this phenomenon has been carried out, so that the facts are now fairly well established. In the present paper these facts are considered with a view to obtaining an adequate explanation of the nature of the diffusion, and a theory is suggested which appears to be consistent with experiment.

In general, the mass of gas passing through a plate of silica increases as the driving pressure and also, very rapidly, with the temperature of the silica. Williams and Ferguson⁽¹⁾ concluded, from experiments at three different temperatures, that in the case of helium the rate of diffusion (μ) varied with the temperature (T) in accordance with the equation

$$\mu = Ce^T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The position of the points on their graph of $\log \mu - T$ suggests, however, that this graph might be somewhat curved so that (1) may not be strictly true. Williams and Ferguson found also that the surface devitrification of the silica was without any pronounced effect on its permeability. They do not offer any explanation of the nature of the diffusion, but conclude, from a comparison of the permeabilities for helium and hydrogen, that the phenomenon cannot be an ordinary effusion of the gas through narrow holes in the silica.

Elsev⁽²⁾ showed that silica is permeable by helium, but not by hydrogen at room temperatures. At this temperature μ is extremely small, and the gas could only be detected spectroscopically in his experiments. No quantitative results were obtained.

Van Voorhis⁽³⁾ measured the permeability of different types of glass and found that the permeability varied very greatly from one specimen to another, being greater the greater the silica-content of the glass. He measured μ at temperatures of 200° C., 300° C., 400° C., and 500° C., and showed that it increased very rapidly with temperature. His results are not consistent with equation (1), however,

* Communicated by the Author.

the experimental variation of μ with T not being sufficiently rapid.

The diffusion of helium, neon, argon, nitrogen, and oxygen through a silica tube 0.33 mm. in thickness has recently been investigated by T'sai and Hogness⁽⁴⁾. They found that the rates of diffusion varied very considerably from one gas to another, the diffusion being undetectable in the experiments with oxygen and nitrogen, and in those with argon, too small to afford quantitative measurements. For helium and neon, however, the rates of diffusion were measurable over a wide range of temperatures; the rate for helium was about 30 times that for neon. T'sai and Hogness found that the variation of μ with T over a temperature range from 180°C. to 980°C. could not be represented by the simple equation of Williams and Ferguson. On plotting $\log \mu$ against T , the resulting graphs show a very decided curvature of the same type as that found by Van Voorhis. They observed, further, that different specimens of silica gave slightly different values for the permeability, and ascribed these variations to the previous heat treatment of the specimens. They suggest that the passage of the gas through the silica must take place by diffusion along narrow channels which increase in diameter with increasing temperature. However, as the permeability for helium increases forty-fold between 180°C. and 955°C., it is difficult to imagine any expansion of the channels sufficient to account for the greatly increased rate of diffusion of the gas.

Theory.

The experiments discussed above, therefore, indicate that the rate of flow of the gas is proportional to the driving pressure and increases very rapidly with the temperature of the silica. In fused silica there must be innumerable small cracks between adjacent surfaces of small crystals, etc., and it is along these very narrow channels that the gas probably moves. Since the width of the channels must be very small in comparison with the free path, it might be expected that the gas would diffuse in accordance with Knudsen's⁽⁵⁾ law. However, this cannot be the case. The experiments indicate that only the molecules having a small cross-section are able to pass through the silica, so that the width of the cracks must be comparable with the molecular diameter. The gas atoms in one of these narrow channels must, therefore, be under the influence of the fields of force of the surface atoms of the solid and so will behave, not as free atoms, but as atoms adsorbed on to the crystal surface.

It has been established by Volmer and Estermann⁽⁶⁾, Volmer and Adhikari⁽⁷⁾, Cockcroft⁽⁸⁾, and others, that under suitable conditions atoms adsorbed on to a solid surface are not permanently fixed in position, but are able to move slowly over the surface of the solid. Thus a gas atom may enter one of the minute cracks and then move along the crack as an adsorbed atom.

Lennard-Jones⁽⁹⁾ has recently given a kinetic theory of this diffusion over the surface of a crystal, and has shown how the theory gives a very satisfactory explanation of the slow absorption of hydrogen by copper as investigated by Ward⁽¹⁰⁾. The surface of the copper used contained many narrow cracks, and Lennard-Jones considers the absorption to be due to the hydrogen atoms, previously adsorbed on to the outer surface of the copper, diffusing laterally into these cracks. The absorption thus takes place in two distinct steps: first, the adsorption of the hydrogen on to the copper surface; second, the diffusion of these adsorbed atoms into the cracks.

It is shown in the following that, in the passage of the inert gases through silica, it is improbable that the absorption of the gas takes place in accordance with the above suggestion. Instead, the gas appears to enter the cracks in the silica without previous adsorption, so that there is an important difference between the two cases. In one the gas can only penetrate into the cracks after previous adsorption on the outer surface of the solid, so that the rate of diffusion is dependent on the amount of the adsorption; in the other this adsorption becomes relatively unimportant, the atoms entering the solid directly from the gas phase.

Lennard-Jones points out that the surface of a crystal must be periodic in structure, being divided into a system of similar cells. Consequently the force binding an adsorbed atom to the surface will depend on the exact spot in a unit cell to which it is attached; being a maximum at one point in each cell and a minimum at some other point. Normally an adsorbed atom will vibrate about a position of minimum potential energy, the amplitude of its vibration increasing with its energy. However, if it acquires an amount of energy greater than a definite minimum (E_0 , say), Lennard-Jones shows that it may leave its equilibrium position and move over the surface of the solid until it loses energy by collision with another atom or otherwise.

The adsorbed atoms may be divided therefore into two classes: the vibrating atoms, which are vibrating about a fixed position of equilibrium, and the mobile atoms, which have sufficient energy to diffuse over the surface.

The adsorbed atoms have been shown to obey the ordinary diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

n = number of adsorbed atoms per sq. cm.

D = coefficient of diffusion,

$$= \frac{1}{2} \gamma l^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where l = average distance travelled by an atom before deactivation,

γ = the number of times an adsorbed atom is raised to the mobile state per second.

We may now apply this theory to the diffusion of a gas through a solid plate, such as a plate of fused silica. Such plates will contain small cracks between the individual crystals, so that if one side A is in contact with a gas at pressure p and the other side B is in a vacuum, there will be a diffusion of the gas atoms from the side A to the side B.

Consider the diffusion along one of these cracks, whose length is taken as the direction of the x axis, the origin being on the surface A of the plate. The number (n) of adsorbed atoms per sq. cm. will vary along the length of the crack, being a maximum (n_0) on the surface A and a minimum (zero) on the surface B. Let the number at a distance x cm. along the crack be n and let the total length of the crack be d cm., so that

$$n = n_0 \quad \text{when } x = 0$$

$$\text{and} \quad n = 0 \quad \text{when } x = d.$$

Then when a steady state is established

$$\frac{\partial n}{\partial t} = 0 = D \frac{\partial^2 n}{\partial x^2}$$

by equation (2), so that

$$n = n_0 \left(1 - \frac{x}{d} \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the number of molecules passing through per second

$$= -SD \frac{\partial n}{\partial x} = \frac{SDn_0}{d},$$

where S is the perimeter of the channel.

The total mass of gas passing through a plate 1 sq. cm. in area will be

$$\mu = \text{constant} \times Dn_0 = ADn_0. \quad . \quad . \quad . \quad (5)$$

Now in the case of the adsorption of the rare gases at high temperatures the concentration of adsorbed atoms is small, so that the number of collisions between the gas atoms on the surface will be small, and the mobile atom will usually have its free path ended by interaction with the atoms of the solid. Under these circumstances Lennard-Jones has shown that the coefficient of diffusion, D , may be written

$$D = \frac{1}{2} \bar{c} l^2 = \frac{\bar{c}^2 \tau_0}{2} e^{-E_0/kT}$$

where

$$\bar{c} = c_0 + \left(\frac{\pi kT}{2m} \right)^{\frac{1}{2}} e^{mc_0^2/2kT} \text{erf} (c_0 \sqrt{m/2kT})$$

= average velocity of the mobile atoms along the surface,

τ_0 = period of vibration of an adsorbed atom normal to the surface,

$E_0 = \frac{1}{2} mc_0^2$ = the energy which must be acquired by an adsorbed atom before it becomes mobile.

Hence by (5)

$$\mu = \frac{A n_0 \bar{c}^2 \tau_0}{2} e^{-E_0/kT} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If E_0 is large compared with kT , $\bar{c}$ becomes equal to c_0 , which is a constant for any specified gas and surface. If, however, E_0 is small compared with kT , as in the case of the adsorption of the inert gases on silica, then

$$\bar{c} = \left(\frac{\pi kT}{2m} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus for any case in which $E \gg kT$, we have

$$\mu \propto n_0 e^{-E_0/kT}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

while for a case in which $E \ll kT$,

$$\mu \propto n_0 T e^{-E_0/kT} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In his experiments on the absorption of hydrogen in copper, Ward⁽¹⁰⁾ measured both μ and n_0 experimentally at a number of temperatures. His results are in complete agreement with the theory of Lennard-Jones.

The concentration (n_0) of adsorbed atoms on the surface was not measured, however, in the experiments on the diffusion through silica. Hence the expressions (8) and (9) for the variation of μ with T cannot be tested without further examination of n_0 itself. This quantity is the equilibrium concentration of the adsorbed atoms on the surface of the solid plate and is given at any temperature by the Langmuir isotherm.

$$n_0 = \frac{c_1 c_2 p}{1 - c_2 p} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The quantities c_1 and c_2 are functions of the temperature which are not determined satisfactorily by adsorption theory. However, from an analysis of the experimental data available, Zeise⁽¹¹⁾ has shown that they may usually be written in the form

$$\begin{aligned} c_1 &= a - bT, \\ c_2 &= c/T^5, \end{aligned}$$

a , b , and c being constants.

Hence

$$n_0 = \frac{\frac{c(a-bT)p}{T^5}}{1 - \frac{cp}{T^5}}$$

and

$$\mu \propto \left\{ \frac{\frac{c(a-bT)p}{T^5}}{1 - \frac{cp}{T^5}} \right\} \bar{c}^2 e^{-E_0/kT} \quad . \quad . \quad (11)$$

This equation may now be applied to the diffusion of the inert gases through silica. The amount of the adsorption of these gases at ordinary or high temperatures is extremely small. Kälberer and Marks⁽¹²⁾ show that at -22°C ., 0°C ., and $+60^\circ \text{C}$., isotherms for the adsorption of argon on silica remain linear up to a pressure of one atmosphere. Hence for this adsorption $c_2 p$ is negligible in comparison with unity, so that the equation (10) becomes

$$n_0 = c_1 c_2 p = \frac{(a-bT)}{T^5} cp. \quad . \quad . \quad . \quad (12)$$

Calculations from the experimental data of Kälberer and Marks indicate that this expression gives the correct temperature variation of n_0 , so that Zeise's results will be applicable in this case.

Further, the inert gases adsorbed on to a surface are held there by the van der Waals's forces, which are relatively weak. Consequently in experiments at high temperatures $E_0 \ll kT$, so that by (6)

$$\bar{c} = \left(\frac{\pi kT}{2m} \right)^{\frac{1}{2}}.$$

On substituting the above expressions for n_0 and $\bar{c}$ in (11) we find

$$\begin{aligned} \mu &= \frac{c(a-bT)}{T^5} \cdot \frac{\pi kT}{2m} \cdot p \cdot e^{-E_0/kT} \\ &= \text{constant} \times \frac{p(a-bT)}{T^4} e^{-E_0/kT}. \quad (13) \end{aligned}$$

Thus the rate of diffusion should be proportional to the pressure and to $\frac{(a-bT)e^{-E_0/kT}}{T^4}$. Experimentally it is found

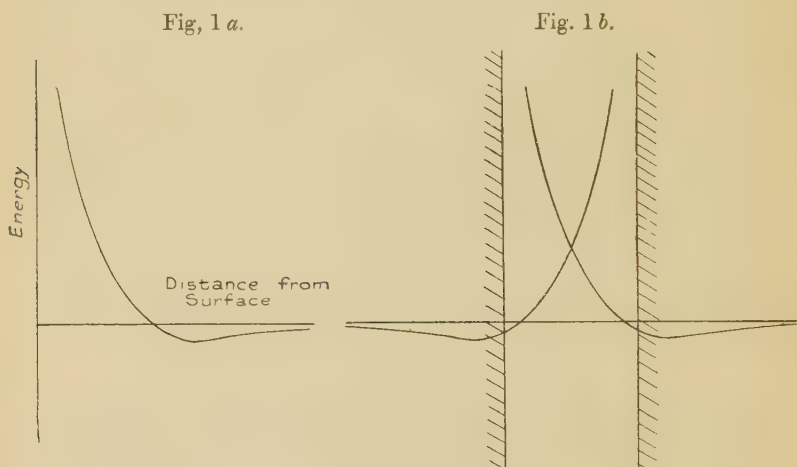
that the variation with pressure is correct, but that that with temperature is incorrect, as the mass diffusing varies more rapidly than the rate predicted above. Therefore, it appears that the diffusion of the inert gases through silica does not take place in accordance with the theory of surface adsorption followed by subsequent diffusion. The reasons for this are discussed below, and an extension of the theory to cover this type of experiment is suggested.

In deriving his expression for the diffusion coefficient of adsorbed atoms, Lennard-Jones assumes that the cracks are so wide that the potential fields due to the two sides of the crack do not overlap so that the diffusion along the two sides proceeds independently. In the case of the diffusion through silica this assumption does not appear to be valid. As has already been stated, the diffusion of argon was not detectable except at the highest temperatures. We may therefore assume that at the highest temperatures the width of the cracks is comparable with the diameter of the argon atom, *i. e.*, about 3.6 Å.U.⁽¹³⁾

Now Lennard-Jones⁽⁹⁾ has shown that the equilibrium distance from the surface for an argon atom adsorbed on a crystal of KCl is 3.61 Å.U., so that if the equilibrium distance on silica is of the same order of magnitude it is comparable with the crack width itself. Hence in this case the potential energy curves for the two sides of the crack will overlap. Suppose that the curve for one side of the crack is represented by fig. 1 *a*, then for openings of the

width under consideration the two curves overlap as in fig. 1 *b*.

The final potential energy curve inside the channel must be compounded from these two. It seems that an atom approaching such an opening will be repelled from both sides and so will not be able to enter unless its velocity normal to the surface is great enough to overcome this repulsive force. Once the atom has entered the crack it will find itself in a channel in which the potential energy distribution is periodic in structure, and the conditions will be favourable for the kind of diffusion suggested by Lennard-Jones. Thus the passage of gases at high temper-



Potential energy curves in a narrow channel.

atures through narrow cracks of molecular dimensions, will be independent of the amount of adsorption on the surface and will depend only on the velocity of the surface diffusion itself.

The rate of diffusion of the inert gases through silica is extremely slow, so that the diffusion will have very little effect on the equilibrium concentration just inside the entrance to the channel. This concentration may therefore be obtained from Boltzmann's law. If W_0 is the work done in transferring a gas atom from the gas to the narrow channel and N is the number of atoms per c.cm. in the gas, then the concentration n_0 just inside the channel will be

$$n_0 = N e^{-W_0/kT}.$$

Now by equation (9) we have

$$\mu \propto n_0 T e^{-E_0/kT} = K N T e^{-(W_0 + E_0)/kT},$$

where K is a constant.

But, if p is the pressure of the gas,

$$p = kNT,$$

so that

$$\mu = B p e^{-(W_0 + E_0)/kT}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

if

$$B = \frac{K}{k}.$$

A comparison of (13) and (14) indicates that the two methods of diffusion, viz., diffusion from an adsorbed layer and diffusion directly from the gas phase, will have different temperature coefficients, so that a knowledge of μ as a function of the temperature will enable a choice to be made between them for any particular case. For the diffusion through silica the work of Van Voorhis and of T'sai and Hogness will be used. Their results are given in the following table :—

TABLE I.

Van Voorhis.		T'sai and Hogness.			
Helium.		Helium.		Neon.	
T° C.	μ .	T° C.	$\mu \times 10^4$.	T° C.	$\mu \times 10^4$.
200	0.188	180	3	520	0.45
300	0.644	310	9	585	0.70
400	1.904	440	21	655	1.10
500	4.274	535	33	760	1.85
		585	42	890	3.15
		650	51	980	4.20
		770	72		
		880	94		
		955	113		

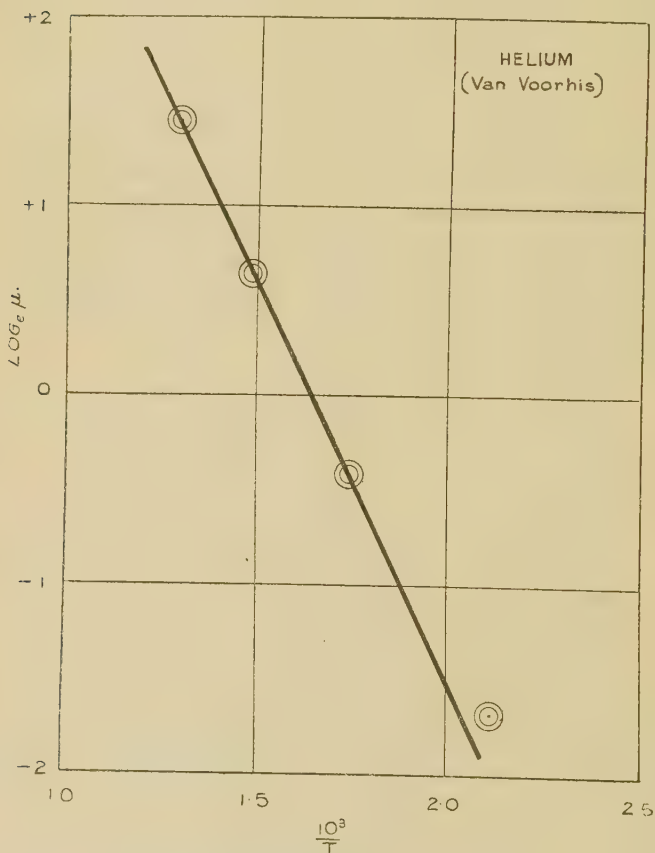
In all cases μ is measured in cubic millimetres per hour per square centimetre passing through a wall of thickness one millimetre.

It appears from equation (14) that

$$\log \mu = \log Bp - (W_0 + E_0)/kT.$$

Consequently $\log \mu$ was plotted against $1/T$, the resulting graphs being shown in fig. 2, fig. 3, and fig. 4. It will be seen therefrom that the experimental data are in agreement with the assumption that the atoms enter the narrow cracks directly from the gas without previous adsorption.

Fig. 2.

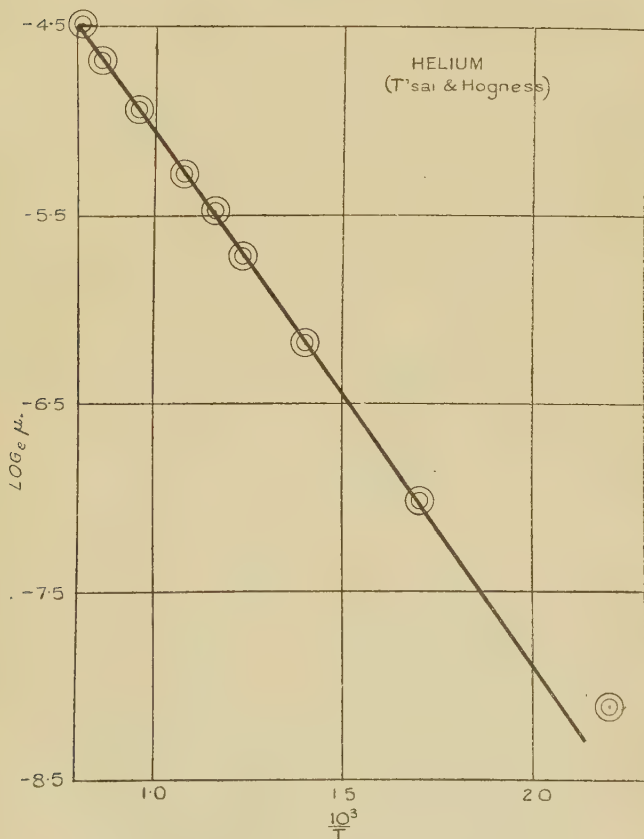


Variation of permeability with temperature.

The general conclusion would therefore appear to be that diffusion after dissociation, as in Ward's experiments, takes place from the adsorbed film. Diffusion of the inert gases into narrow cracks whose widths are comparable with the dimensions of the unit cell of the crystal lattice, takes place

directly from the gas phase. This penetration of gas atoms into minute cracks must be almost indistinguishable from true lattice diffusion, *i. e.*, diffusion into the crystal lattice itself. It is possible that in the case under consideration

Fig. 3.



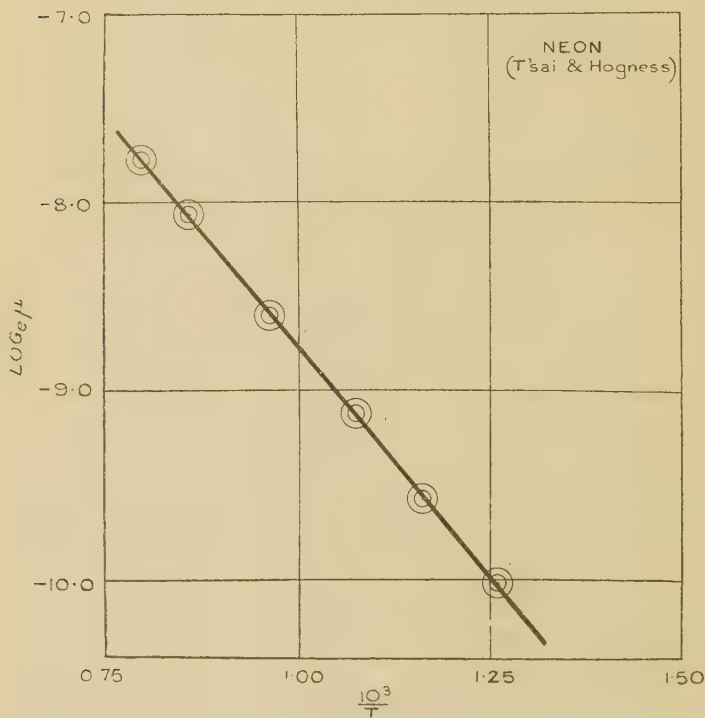
Variation of permeability with temperature.

the inert gases are able to penetrate through the silica crystals themselves as well as along the narrow cracks between these crystals.

It is of interest to calculate the activation energies ($W_0 + E_0$) from the above graphs. The values found from the data of T'sai and Hogness are 5570 cal./gram-atom for

helium and 9460 cal./gram-atom for neon. These figures refer to the passage of the two gases through the same silica tube. The energy of activation obtained from Van Voorhis's data is 8110 cal./gram-atom for the diffusion of helium through pyrex. These energies of activation are difficult to explain except on the basis of the superposition of the potential fields of the two walls of the crack. The

Fig. 4.



Variation of permeability with temperature.

energy of adsorption of the inert gases held by van der Waals's forces is small, being in general of the order of 1000 cal./gram-atom. This is the energy required to remove them completely from the surface. That required to activate them to the mobile state therefore should be considerably less than this.

Further information regarding the magnitude of the energy E_0 may be derived from figs. 2, 3, and 4. It will

be remembered that equation (14) is valid only so long as kT remains very large in comparison with E_0 . Consequently the graph of $\log \mu - \frac{1}{T}$ will be linear only so long as $kT \gg E_0$. For experiments conducted at low temperatures, this inequality will probably not be satisfied in the case of the inert gases, so that the linear relation between $\log \mu$ and $\frac{1}{T}$ would be expected to fail at low temperatures. The results of both Van Voorhis and of T'sai and Hogness indicate that this is the case. It will be seen that the points representing Van Voorhis's result at 200° C. and T'sai and Hogness's result at 180° C. both lie above the straight line graphs, as would be expected when $kT \gg E_0$. Experiments were not conducted at temperatures lower than 180° C., so that only one point off the straight line is obtained in each case; but the two results agree remarkably well in showing that the temperature at which kT begins to be comparable with E_0 is about 200° C. Both experiments indicated that at 300° C., $kT \gg E_0$, so that it must follow that for the activation of helium on silica

$$E_0 \ll 1150 \text{ cal./gram atom.}$$

This value is of the correct order of magnitude if the forces between the gas atoms and those of the solid are of the van der Waals's type only.

In the case of neon the permeability was so low that experiments were not made at temperatures below 520° C. The graph shows no deviation from the straight line at this temperature so that for this case we can only say that the energy of activation must be very considerably less than 1600 cal./gram-atom.

If the gas atoms enter directly from the gas, the energy W_0 represents the work done in driving the atom into the narrow channel against the repulsive forces of the walls. The nature of W_0 on this view is therefore very different from that of the energy of activation E_0 .

Another example of the above type of diffusion appears to be provided by the experiments of Rideal and Wilkins⁽¹⁴⁾ on the low pressure oxidation of copper. They found that the amount of oxygen passing through the cracks in the film of oxide was proportional to the pressure of the gas and had a temperature coefficient of the form $e^{-E_0/kT}$. The rate of diffusion is thus proportional to $pe^{-E_0/kT}$, but is not proportional to the concentration of adsorbed oxygen on the

oxide surface, since this concentration itself will vary rapidly with the temperature. The passage of the oxygen through the oxide therefore conforms to equation (14) rather than to equation (13). A comparison of the work of Rideal and Wilkins with that of Ward therefore seems to indicate that while hydrogen diffuses into copper only after previous adsorption on its surface, oxygen diffuses through a copper oxide film without previous adsorption.

Summary.

It is suggested that the passage of the inert gases through fused silica is due to the diffusion of adsorbed atoms along narrow cracks in the silica. The experimental data are reviewed and shown to be consistent with this theory.

It appears that the gas atoms enter the cracks directly from the gas phase rather than from the layer of gas adsorbed on the surface of the silica.

References.

- (1) Williams and Ferguson, *J. A. C. S.* xlv. p. 2160 (1922).
- (2) Elsey, *J. A. C. S.* xlviii. p. 1600 (1926).
- (3) Van Voorhis, *Phys. Rev. A*, xxiii. p. 557 (1925).
- (4) Tsai and Hogness, *J. of Phys. Chem.* xxxvi. p. 2595 (1932).
- (5) Knudsen, *Ann. d. Phys.* xxviii. p. 104 (1909).
- (6) Volmer and Esterman, *Z. Phys.* vii. p. 13 (1921).
- (7) Volmer and Adhikari, *Z. Phys.* xxxv. p. 170 (1925).
- (8) Cockcroft, *Proc. Roy. Soc. A*, cxix. p. 293 (1928).
- (9) Lennard-Jones, *Trans. Faraday Soc.* xxviii. p. 333 (1932).
- (10) Ward, *Proc. Roy. Soc. A*, cxxxiii. p. 506 (1931).
- (11) Zeise, *Z. Phys. Chem. Abt. A*, cxxxviii. p. 289 (1928).
- (12) Kälberer and Mark, *Z. Phys. Chem. Abt. A*, cxxxix. p. 151 (1928).
- (13) Jeans, 'Dynamical Theory of Gases,' p. 327.
- (14) Rideal and Wilkins, *Proc. Roy. Soc. A*, cxxviii. p. 394 (1930).

LXXXII. *The Diffusion of Mercury on Rolled Tin Foils.* By F. W. SPIERS, *B.Sc.**

Introduction.

THIS work was undertaken at the suggestion of Prof. W. Gerlach as a continuation of some observations made by him on the diffusion of mercury drops on rolled tin foil. A short preliminary description of the phenomenon was published by Prof. Gerlach in 1930 ⁽¹⁾,

* Communicated by Prof. R. Whiddington, F.R.S.

and a short account of the earlier experiments has been published by the writer ⁽²⁾. The diffusion of mercury into the tin foil gives rise to an amalgam rich in tin, and the object of the following experiments is to determine the nature of this amalgam and to relate it to the properties of the tin-mercury system.

The Diffusion Phenomenon.

A mercury drop (*e. g.*, 5–10 mg.) placed upon tin foil remains spherical for a few seconds owing to surface impurities, and then sinks right through the foil, spreading into a small mercury well. From this the mercury diffuses into the surrounding tin, and its progress is easily observable by the contrasted appearance of the amalgam which forms and the smooth tin foil. The diffusion is rapid at first but not unlimited, and after a period of a few hours ceases, leaving a well-defined area of amalgam. The border between the amalgam and the tin is very sharp and accurately elliptical, the major axis being parallel to the direction of rolling of the foil. The amalgam, although soft initially, soon hardens into a brittle solid. As there is an increase in the quantity of matter inside the elliptical border the amalgamated foil puckers, and if the foil is particularly smooth the puckering takes the form of regular concentric elliptical folds.

After the diffusion is complete the mercury is regularly distributed through the ellipse, as was indicated by spectroscopic analysis of different parts of the ellipse ⁽¹⁾ and by X-ray shadow photographs. A series of such photographs taken at frequent intervals during the diffusion showed that the mercury-well at the centre disappeared when the ellipse had attained about 70 per cent. of its final size.

The diffusion of a number of mercury drops of different mass was observed, and the dimensions of the ellipses were determined during the diffusion. The eccentricity of the ellipse was found to be independent of the mass of the drop and constant during the growth. The area included by the elliptical border, *i. e.*, the mass of tin amalgamated, was proportional to the mass of the drop. The mass per sq. cm. of the foil and the mass of mercury combining with it were measured and the atomic

percentage* of mercury inside the ellipse calculated. The experiments were repeated with a number of foils of different thickness, and the composition of the amalgam determined in each case. The results are given in Table I., from which it will be seen that for a considerable variation in the mass of the drop and thickness of foil used the atomic percentage of mercury is almost constant. It was considered possible that this constant composition obtained by diffusion corresponded with the formation of an intermetallic compound. This point will be dealt with later; here it is evident, however, that the mean compo-

TABLE I.

	Thickness of foil (μ).	Axial ratio.	Mass of Hg drop.	Atomic percentage of Hg in amalgam
1	10.5	1.10	2.33 mg.	11.6
			4.04	12.0
			5.05	11.4
			11.32	11.9
			16.18	11.7
2	7.7	1.20	9.68	11.7
3	16.5	1.09	14.6	11.8
			28.7	11.9
4	46.4	1.10	27.7	12.2
			57.7	11.9
5	11.0	1.60	13.8	11.8
			22.0	12.1
Mean Atomic percentage Hg content = 11.8 ± 0.4 .				

sition 11.8 per cent. Hg does not coincide with any simple chemical formula, but lies between the formulæ HgSn_7 and HgSn_8 .

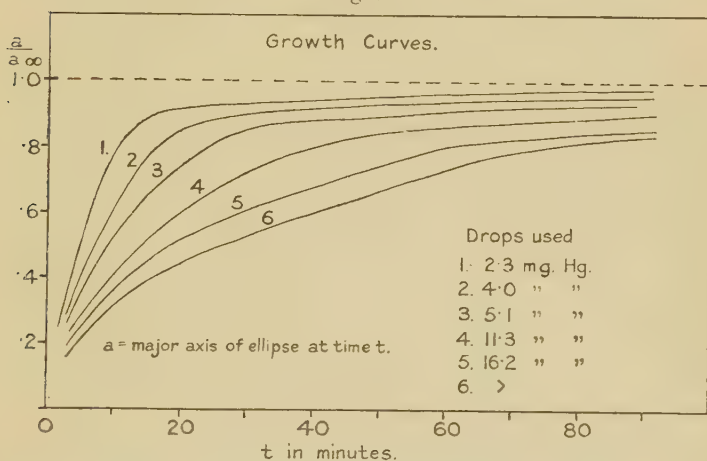
Curves of growth were also determined for a range of mercury drops on the same foil, and although too many indeterminate factors prevented an exact analysis of the results, an approximate interpretation was obtained. For each ellipse examined the diffusion could be represented approximately by two e -functions of the form $A = A_{\infty}(1 - e^{-kt})$, A_{∞} being the final area of the ellipse. The first function described the growth as long as the mercury reservoir existed at the centre of the ellipse, the value

* Atomic percentages are used throughout this paper.

of k depending inversely on the mass of the drop. The second function, with k almost the same for all drops, held for the latter part of the diffusion after the disappearance of the reservoir. Qualitatively it appears that the mercury-well exerts a hydrostatic pressure which accelerates the diffusion, and that after its disappearance a slower diffusion takes place between the excess mercury and the surrounding tin. The curves of growth and their analyses are given in figs. 1 and 2; the above interpretation does not hold for very large drops.

The elliptical diffusion of the mercury is conditioned by the rolling of the foil, as was shown by diffusion

Fig. 1.



experiments on thin lead strips rolled in the laboratory. The crystallites of the foil are elongated in the direction of rolling, and this fact is sufficient to account for the elliptical diffusion. Assuming that the mercury diffuses uniformly in all directions inside a single crystal, the only hindrance to its progress will be due to impurity layers between the crystallites. Owing to the elongation of the crystallites the number of impurity layers encountered per cm. will be less, and hence the speed of diffusion greater, in the direction of rolling than at right angles to it.

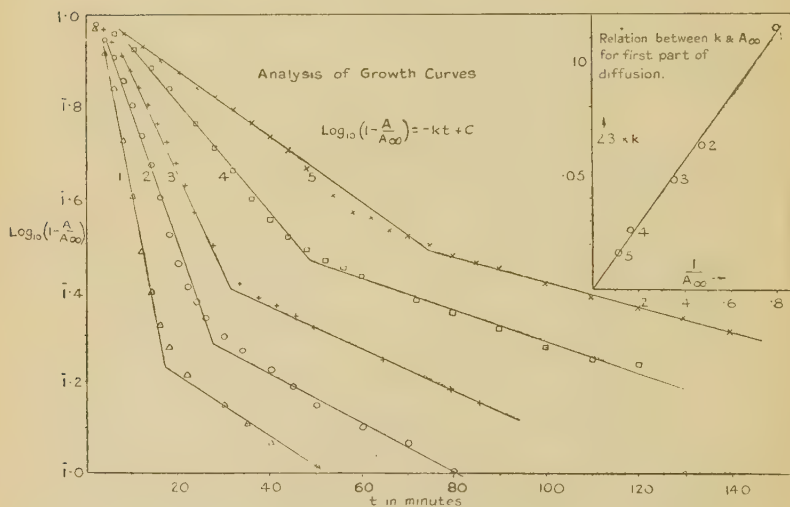
X-ray Examination of the Amalgam.

Simson ⁽³⁾ has shown that a phase exists in the tin-mercury system which has a crystal structure other than

that of tin. Mercury appears to be soluble to the extent of 1 per cent. in the tetragonal tin lattice, while between 1 per cent. and 8 per cent. mercury content a second phase, possessing a hexagonal crystal structure, is present side by side with the original tetragonal phase. Beyond 8 per cent. this hexagonal structure is the only solid phase present and was observed by Simson as far as 35 per cent. Hg content. The cell given contains one atom, and has dimensions

$$a=3.18 \text{ \AA.}, \quad c=2.99 \text{ \AA.}, \quad \frac{c}{a}=0.940;$$

Fig. 2.



no change of lattice constant with varying Hg content was reported.

The first experiments in this investigation were made to compare the structure of the amalgamated foil with that of tin. Powder photographs were obtained by pressing the powdered amalgam on to a thin glass slip and setting this at a small angle to a slightly diverging beam of filtered $K\alpha$ radiation of copper. Powdered amalgam was pressed on the upper part of the glass slip, powdered tin on the lower, interference of the two sets of reflexions on the plate being avoided by means of a thin aluminium baffle fixed on the plate-holder at right angles

to the plane and axis of the slip. Using the tin lines for calibration, the measurements of the amalgam lines were independent of the plate distance, and any errors due to inaccuracy of setting of the glass slip could be traced and corrected.

No indication of the tin lattice was observed on the amalgam photographs, and measurement of the reflexions lead to the cell given by Simson. A Debye-Scherrer photograph of the amalgam alone was taken with a cylindrical camera in order to measure as many reflexions as possible. Eighteen lines were recorded in complete agreement with a hexagonal cell of the following dimensions :—

$$a=3.23 \text{ \AA.}, \quad c=3.00 \text{ \AA.}, \quad \frac{c}{a}=0.931.$$

These dimensions, however, were determined with a plate camera by comparing the (100) and (001) reflexions with those from the (200) and (101) tin planes. No spectra are missing, and the intensities appear normal for a cell with atoms only at its corners; a rough determination of the density also indicated that this cell could only accommodate one atom.

The atoms of the hexagonal lattice can be described as two interpenetrating body-centred orthorhombic lattices having origins at (000) and $(\frac{1}{2}0\frac{1}{2})$, and dimensions

$$a=6.00 \text{ \AA.}, \quad b=5.60 \text{ \AA.}, \quad c=3.23 \text{ \AA.}$$

The closeness of this arrangement to that of the tetragonal tin can be seen from the figures given by Mark and Polanyi ⁽⁴⁾. The tin atoms are described by two body-centred tetragonal lattices with origins at (000) and $(\frac{1}{2}0\frac{1}{4})$ and dimensions

$$a=b=5.84 \text{ \AA.}, \quad c=3.16 \text{ \AA.}$$

Simson observed this hexagonal lattice up to 35 per cent. Hg, and if the mercury were soluble to anything like this extent in the lattice a change in the parameter should occur. Accordingly a few photographs were taken to compare the principal spacings from a number of amalgams of varying compositions with those from a standard amalgam taken from an ellipse. Over the range 8–25 per cent. Hg no change greater than $\frac{1}{4}$ per

cent. was detected, this figure representing the order of accuracy of the measurements.

Density Considerations.

Since the volume V of the unit cell is constant over the range 8–25 per cent. Hg and only one lattice is present, the density of any amalgam of composition x per cent. may be calculated if the assumption is made that all the atoms lie on the lattice. The density is

$$\rho = \frac{1.66 \bar{A}}{V}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A is the average atomic weight for the mixture of atoms in question and V is in cubic Ångströms.

Between 1 per cent. and 8 per cent. both tetragonal and hexagonal lattices are present; hence, if these have volumes V_T and V_H per atom the density will be given by

$$\rho = \frac{100 \bar{A}}{n_T V_T + n_H V_H}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

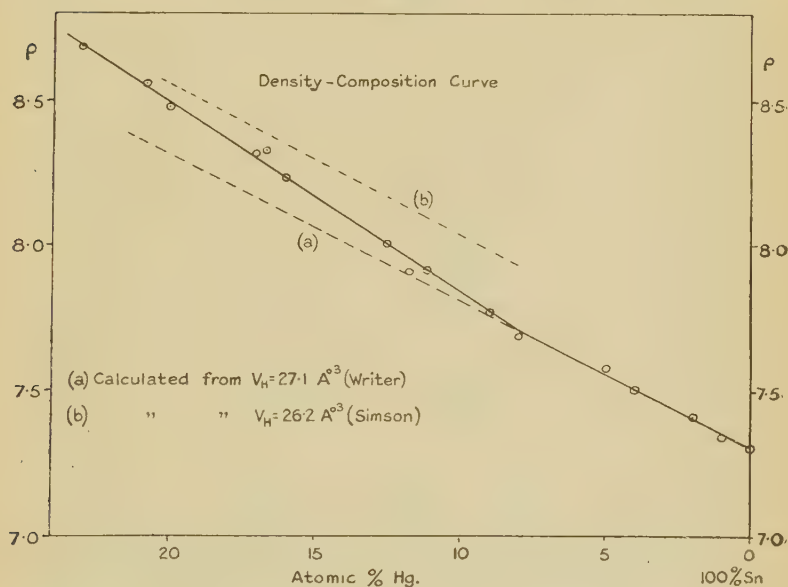
where n_T and n_H are the percentage numbers of atoms on the two lattices. The values $V_T = 26.9 \text{ Å}^3$ (Mark) and $V_H = 27.1 \text{ Å}^3$ (writer) are so close that they may be taken as equal, and hence, since $n_T + n_H = 100$, the expression (2) reduces to (1), which should then cover the experimental densities with sufficient accuracy.

Accordingly the densities of a number of amalgams were determined and compared, as in fig. 3, with the values obtained by equation (1). The experimental and calculated densities agree as far as the composition 8 per cent. Hg, beyond which the experimental curve rises much more steeply than expected on the above considerations. Over this range of compositions V has been shown to be constant, and since an error in the absolute value of V would affect the position but not the slope of the density line the observed change in slope must be due to a second phase of high density. Since the hexagonal phase is the only solid one observed in this region the second phase must be a liquid one, namely, a slight solution of tin in mercury. The existence of this liquid phase was easily demonstrated. By pressing an amalgam block, containing more than 8 per cent. Hg, on a sheet of clean tin foil

a small patch of amalgamated foil would appear in the course of a few seconds.

It will be noticed that the cell given by Simson has an a -axis slightly less than that obtained by the writer, and consequently a smaller cell volume, which does not fit in so well with the density measurements. In this case the volume $V_H=26.2 \text{ \AA}^3$ is less than $V_T=26.9 \text{ \AA}^3$, and hence the approximation from expression (2) to (1) for amalgams below 8 per cent. cannot be made. More-

Fig. 3.



over, n_T and n_H vary with the composition, since the tetragonal lattice disappears at 8 per cent. Hg, and hence the densities can only be evaluated by making assumptions about the compositions of the two phases present. This would be difficult to do, but in any case the densities so calculated between 0 and 8 per cent. must lie above the experimental values, while beyond this point they follow the line (b) in fig. 3.

Measurements of Electrical Resistance.

The chief investigations of the phase diagram of the Hg-Sn system were made at the beginning of the century

by Puschin⁽⁵⁾ and van Heteren⁽⁶⁾, but there has been no further attempt to alter the diagram to conform with the later results of X-ray analysis. Some resistance-temperature measurements were therefore undertaken in order to investigate the possibility of the formation of an intermetallic compound, and to give also some idea of the phase diagram at the tin end of the system.

The amalgams were made by fusion* under hydrogen and the specimen cast in capillary U-tubes of internal diameter 0.5 mm. The specimens were cooled inside the furnace, a small temperature gradient allowing the amalgam to solidify from the bottom of the U-tube upwards, drawing in more molten metal as it did so and avoiding strains set up by contraction on freezing. A number of specimens of varying composition were mounted in an oil-bath fitted with heating and stirring arrangements. Relative values of the resistances were measured at different temperatures by a potentiometer method, all the specimens being subjected to identical heat treatment throughout.

Finally the specimens were analyzed by evaporating off the mercury *in vacuo*, each side of the specimen being analyzed separately. In some cases a small composition gradient was found along the specimen, so that these results represent averages over a small composition range; the variations, however, are not serious enough to affect the general results.

Measurements for repeated heatings (to 100° C.) and coolings were made until the resistance-temperature curves became completely reversible. The resistance curves for all the specimens were linear up to at least 75° C., and the temperature coefficients α were worked out over this range of temperature. The specimens were then annealed for 60 hours at 140° C., after which further heating and cooling curves were taken. The curves were again reversible, and the values of α were practically identical with those determined before annealing. The value of α determined for a strip of amalgamated foil taken from an ellipse is in good agreement with the other determinations made in that region of composition.

The resistance-temperature curves for specimens containing small percentages of Hg were linear over the

* Distilled mercury and tin, guaranteed 99.9 per cent. pure, were used.

range of temperature investigated. The curves for richer specimens showed marked departure from linearity as 100°C. was approached; the effect, however, was perfectly reversible for the slow rates of heating and cooling used. These deviations indicate the approximate temperatures at which a change of state sets in, since the resistance-temperature relation is linear for an alloy at temperatures sufficiently removed from any transition points. Table II. gives the estimations of T_{solidus} so obtained, together with the values of α for the specimen examined. The amalgams, rich in mercury, were very brittle, and in consequence a few of them developed flaws

TABLE II.

Composition per cent. Hg.	α before annealing.	α after annealing.	T_{solidus} .
0	$4.72 \times 10^{-3}/^{\circ}\text{C.}$	$4.72 \times 10^{-3}/^{\circ}\text{C.}$	231.8°C.
1.1	4.05	3.82	above 100°
2.5	3.57	3.57	" "
7.7	2.78	2.77	" "
8.2	2.65	2.65	85°
8.8	2.60	2.58	78°
10.6	2.29	—	75°
12.4	2.34	2.40	75°
14.3	2.30	—	75°
27.3	2.16	—	75°

during annealing; but the general agreement between the results before and after annealing is sufficiently good to fix the form of the α -composition curve shown in fig. 4.

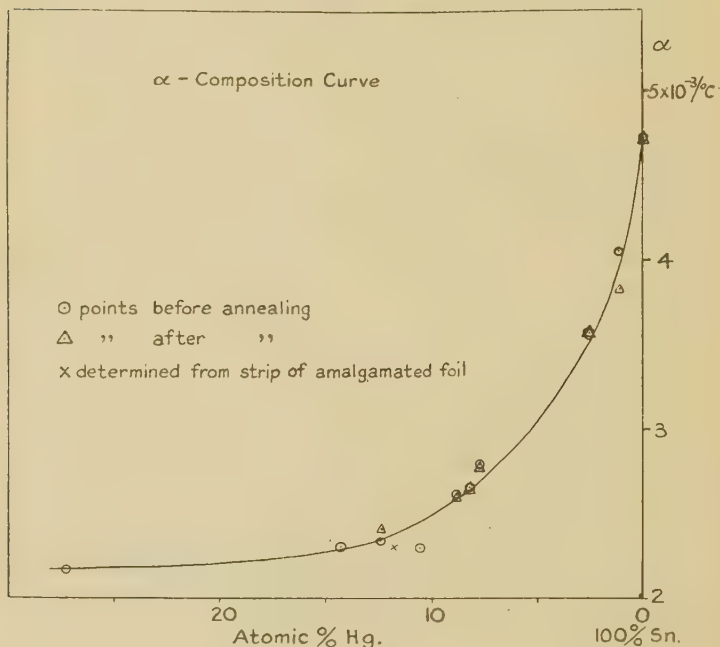
Conclusions.

The α -composition curve shows no peak in the region examined, as would be expected if the hexagonal lattice were an intermetallic compound either of fixed or slightly variable composition. Hence this phase, possessing a crystal structure different from that of the parent element tin, is correctly described as a secondary solid solution.

Fig. 5 shows the liquidus curve for the Hg-Sn system as determined by Puschin ⁽⁵⁾, to which is added a solidus

line suggested by the X-ray results of Simson ⁽³⁾ and the present electrical measurements. The line BE marks the limit of solution of Hg in the tin lattice, as evidenced by the appearance at 1 per cent. Hg of a hexagonal lattice on Simson's photographs, the point B being fixed by the fact that the tin lattice disappears at 8 per cent. Hg. The limit of the solubility of Hg in the hexagonal lattice, CF, is based on the appearance of a liquid phase at and

Fig. 4.

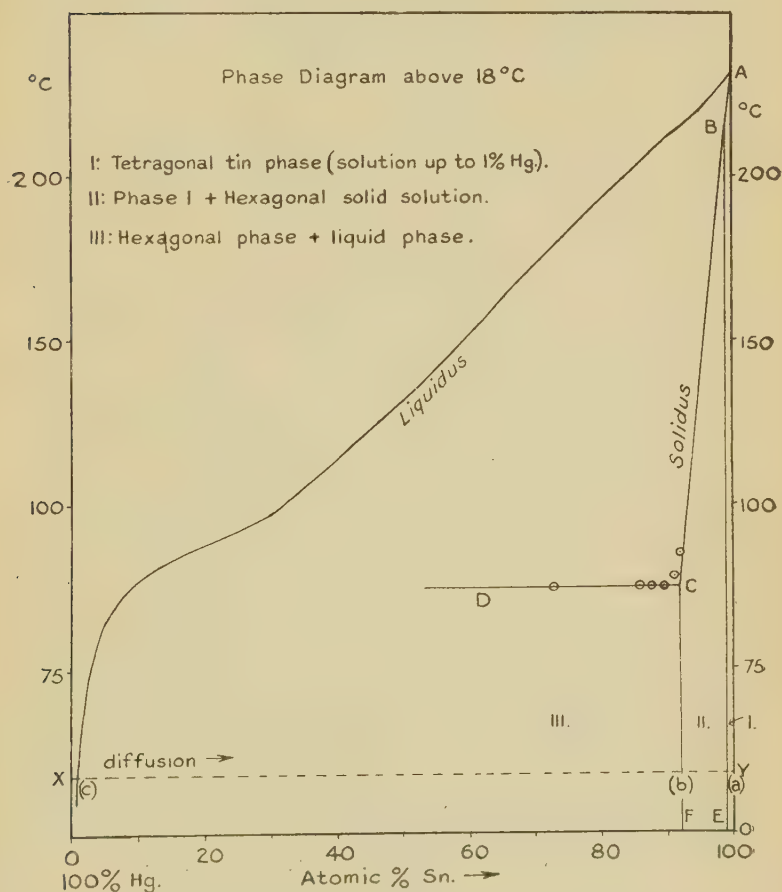


beyond 8 per cent. Hg, as shown by the density measurements, this fitting in with the disappearance of the tetragonal phase and the bending of the solidus line at C.

The diffusion phenomenon corresponds to proceeding along a constant temperature line in the direction XY (fig. 5), equilibrium being established between the solid phase (b) and the liquid phase (c). The equilibrium composition will lie between (b) and (c), and considerations similar to those used in deriving the Phase Rule will show that this composition is fixed for any given tempera-

ture. Omitting the vapour phase and the pressure variable three phases are in equilibrium at the elliptical border. These are : (a) pure tin, (b) the hexagonal solid solution, and (c) a liquid phase—the variables concerned

Fig. 5.



being temperature, the concentrations $\frac{m_b}{V_b}$, $\frac{m_c}{V_c}$ of the mercury, and the concentrations $\frac{s_b}{V_b}$, $\frac{s_c}{V_c}$ of tin in the phases (b) and (c). Here m_b , m_c , s_b , s_c are the actual masses of the mercury and tin, and V_b , V_c the volumes of the phases

present. Hence, including the temperature, there are seven variables. Now there will be two condition equations of the form $f\left(T, \frac{m}{V}, \frac{s}{V}\right)=0$ relating the con-

centrations and temperature for the phases (b) and (c), and three equations representing the equilibrium between the components in the various phases, viz., two for the transference of tin between the phase (a) and phases (b) and (c), and one for the transference of mercury between (b) and (c). As phase (a) is a pure component there can be no transference of mercury between it and either (b) or (c). There are in all five equations of condition and equilibrium, and to these must be added the equation $m_b + m_c = M$, representing the limited mass M of mercury placed on the foil. Hence, if the temperature is given there are six equations to determine the six variables stated above, and in particular the ratio $(m_b + m_c)/(s_b + s_c)$, i. e., the composition of the amalgam inside the ellipse is fixed as observed by experiment.

An attempt was made to detect the effect of temperature on the diffusion limit; as the final stages of growth of the elliptical area are very slow it was considered that any expansion of the ellipse due to long heating would persist for some time after the specimen was removed from the heater. No change was observed after forty hours at 80° C., and a further seven hours at 110° C. produced only $\frac{1}{2}$ per cent. change in the linear dimensions of the ellipse.

The research was concluded at this point, as the investigation of the diffusion phenomenon appeared to be reasonably complete. Mention has been made of the lack of data concerning the phase diagram for the tin-mercury system. A suggestion has been made for the tin end of the diagram, but this work has only been carried as far as was necessary for the determination of the nature of the hexagonal phase and the explanation of the amalgam formed by diffusion.

Summary.

Mercury drops placed on rolled tin foils diffuse into elliptical areas forming an amalgam of approximately constant composition 11.8 per cent. Hg. Various features of the diffusion are described, an empirical interpretation of the curves of growth of the ellipses is given, and the elliptical diffusion explained in terms of the rolling effects.

The crystal structure of the amalgam, determined by X-ray methods, is hexagonal, the unit cell containing one atom and having dimensions $a=3.23 \text{ \AA.}$, $c=3.00 \text{ \AA.}$ According to previous work by Simson the tetragonal tin structure is observable from 0.8 per cent. Hg and the hexagonal lattice from 1.35 per cent. Hg. Density measurements indicate the existence of a liquid phase from 8 per cent. Hg onwards; measurements of electrical resistance show the hexagonal phase to be a secondary solid solution and give an indication of the solidus curve for the tin end of the Hg-Sn system.

The constant composition obtained by diffusion follows from consideration of the equilibrium of the phases present at the elliptical border.

Acknowledgments.

The first part of this work was carried out in Munich, and my warmest thanks are due to Prof. W. Gerlach, not only for help at that time but also for his generosity in allowing me to continue the problem in England. I am much indebted to Prof. R. Whiddington for kindly granting me facilities for the work in his laboratories and to Dr. E. C. Stoner for much helpful discussion.

Finally I would acknowledge gratefully an Exchange Studentship granted by the Anglo-German Academic Board, which made study in Munich possible.

References.

- (1) W. Gerlach, *Sitzungsber. bayr. Akad. d. Wissenschaften*, p. 23 (1930).
 - (2) F. W. Spiers, *Proc. Leeds Phil. Soc.* ii. p. 280 (1932).
 - (3) Cl. v. Simson, *Zeit. phys. Chem.* cix. p. 183 (1924).
 - (4) Mark and Polanyi, *Zeit. f. Phys.* xviii. p. 75 (1923).
 - (5) N. A. Puschin, *Zeit f. anorg. Chem.* xxxvi. p. 201 (1903).
 - (6) W. J. van Heteren, *Zeit. f. anorg. Chem.* xlii. p. 129 (1904).
- East Pgh., Pa.

LXXXIII. The Diffusion of Electrolytes.

To the Editors of The Philosophical Magazine.

GENTLEMEN,—

IN a recent article by R. J. Davies, M.Sc., on "The Diffusion of Electrolytes" (*Phil. Mag.* (7) xv. no. 98, p. 489, Feb. 1933), the author, who has done me the honour of employing the method originally described by

me (Phys. Soc. Proc. xxxvi. p. 313, 1924), states—p. 497—that I used mercury green light, $\lambda 5461 \text{ \AA.}$, for the determination of $d\mu/dl$, and sodium yellow, $\lambda 5893 \text{ \AA.}$, in the measurement of $d\mu/dn$.

I should be glad of the opportunity to correct this statement, as it is difficult to see any object in changing from one monochromatic source to another during the course of an investigation, and indeed I did not do so.

The determination of $d\mu/dn$ was made by means of the Rayleigh interferometer, and for this purpose monochromatic light was not used at all, but, on account of the necessity of identifying the achromatic fringe in the displaced fringe-system, a *white* light source was employed, as clearly stated in Phys. Soc. Proc. xxxvii. p. 117 (1925).

Yours faithfully,

B. W. CLACK.

Birkbeck College,
London, E.C.4.
April 3rd, 1933.

LXXXIV. Notices respecting New Books.

Elementary Mathematics from an Advanced Standpoint. By FELIX KLEIN. Translated by E. R. HEDRICK and C. A. NOBLE. [Pp. ix+274.] (Macmillan, 1932. Price 15s.)

THE book of which this is a translation was originally prepared from manuscript notes of lectures primarily addressed to teachers of mathematics in schools, and much of the spirit of the spoken word has been happily retained. As to subject matter, topics are dealt with which fall in the fields of arithmetic (properties of integers, complex numbers), algebra (equations with real unknowns, and complex parameters), and analysis (logarithmic and trigonometrical functions). The unique value of the book, however, lies not so much in the subject matter as in the manner of presentation; the aim is not to give a complete and systematic account of any branch of mathematics, but to bring the "advanced" treatment, given in varied detail, of selected topics into a historical perspective, and arising from this, to suggest points of view which may influence advantageously the teaching of mathematics in the more elementary stages.

When an honours graduate in mathematics is suddenly plunged into the teaching of the elementary stages of the subject, it is not surprising that he should often fail to find any

relevance in his advanced work for the purpose, and that he should carry on his elementary teaching just as he was taught at that stage—or, in the other extreme, become completely unintelligible to his pupils. Yet the great value of advanced study (in this connexion) is that it may enable those who have benefited by it to see and present the subject, at any stage, influenced by the view gained from the highest peaks they have reached. The ideal is elusive. But Klein's book would help towards its attainment. It will be stimulating not only to teachers of mathematics, but also to the more advanced students, giving them a fuller appreciation of the subject as an integrated, growing whole; and to those scientists, too, who see in mathematics merely a necessary, but sometimes refractory, tool for their own special purposes. Particularly, however, it may perhaps be recommended to those who are experts in the Science of Education. E. C. S.

Lehrbuch der theoretischen Physik. Von Dr. GEORG JOOS.
[Pp. xvi+644.] (Akademische Verlagsgesellschaft m. b. H.:
Leipzig, 1932. Price 26 M.)

FOR theoretical physics, this book is as a guide in mountainous country. The highest peaks which have been reached are not attempted, but heights are attained from which the character of the climb to these may be appreciated; and of the country below, little is missed of the salient features. That so wide a territory should be so quickly covered implies a profound knowledge of the country in the guide, who, though he wisely does not despise well proven routes, has opened up many new ones. A tour inevitably differs from a pioneer exploration; but that some of the fascination of that is lost is perhaps an ungracious criticism. The presentation of a science, particularly the abstracted theoretical side of it, as a rounded system, may be misleading as to its character; but given the proper historical and experimental background, as to the necessity of which the author would undoubtedly agree, this book will be of the utmost value.

It may be strongly commended to those who wish to have a comprehensive, yet succinct and lucid presentation of all the more important sides of theoretical physics. Particularly will it be valuable for those concerned with the teaching of honours students. The plan of the volume, and the choice of subject matter, are excellent. After a mathematical section, which includes an admirable account of vector calculus, enabling vectors to be used throughout the book, the subject matter is divided into six sections, dealing with mechanics, including relativity mechanics; electromagnetism,

from the continuum standpoint—here optical phenomena are treated—and the atomistic; heat, phenomenological and statistical; and the structure of atoms and molecules, with two chapters on quantum mechanics. The account of statistical mechanics, including the Bose and Fermi statistics, is of particular value, as there are so few books which attempt to bridge the gap between an elementary classical treatment and the modern developments. In an appendix are given outlines of solutions of problems which extend the scope of the text, and a list of books for further study.

The cheapness of the book, which is excellently produced, calls for admiring comment. E.C.S.

A Text-book of Physics.—Vol. I. *Mechanics.* By E. GRIMSEHL. Edited by R. TOMASCHEK. Translated from the German by L. WOODWARD. (Blackie & Son Ltd. Price 15s.)

FROM the extensive and interesting selection of practical applications, the range of which may be indicated by mentioning the Eötvös balance, mercury, oil, and diffusion pumps, and even the Flettner rotor-ship and the Sperry gyroscopic stabilizer, it would appear that the chief aim of this book is to link up mechanical principles with realities.

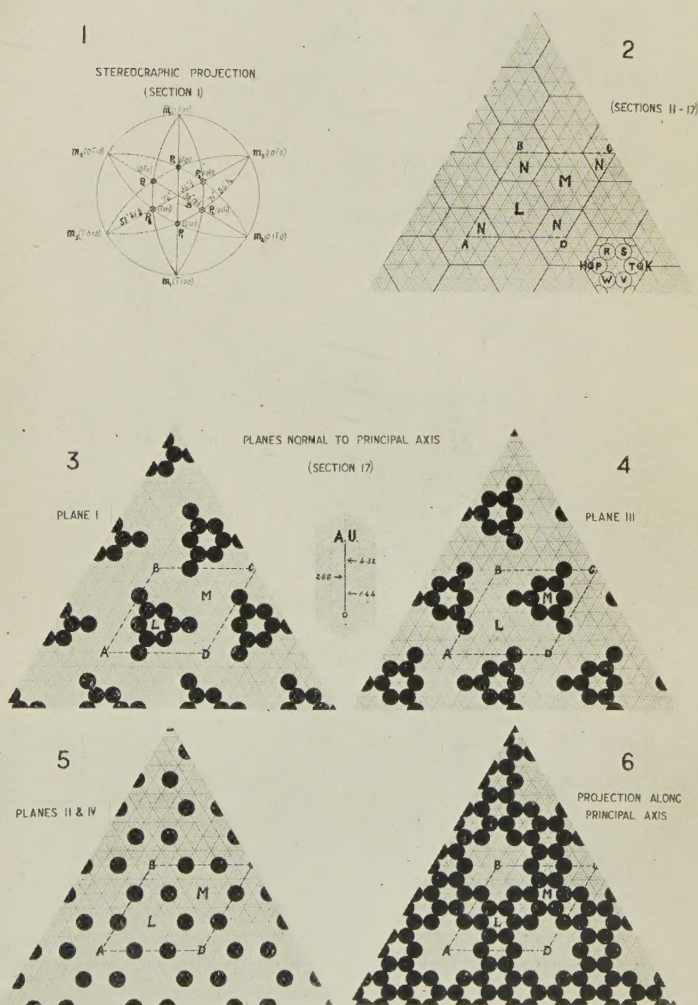
Elementary mathematical methods are employed including some simple calculus, and a good deal of the work is suitable for the first year of a Final Degree Course.

In addition to statics, dynamics, and hydrostatics, much of which will be done by the student before reaching this stage, and other topics usually to be found in books of this nature, there is a rather brief account of the constitution of material bodies, including some remarks on space lattices. The final chapter, on the flow of liquids and gases, embraces a wider range than is usually to be found in a text-book of physics, and concludes with sections on flight, but the mathematical treatment of viscous flow through tubes is reserved for an appendix. No mention is found of damped oscillations or wave motion, but the latter topic is dealt with in Volume II.

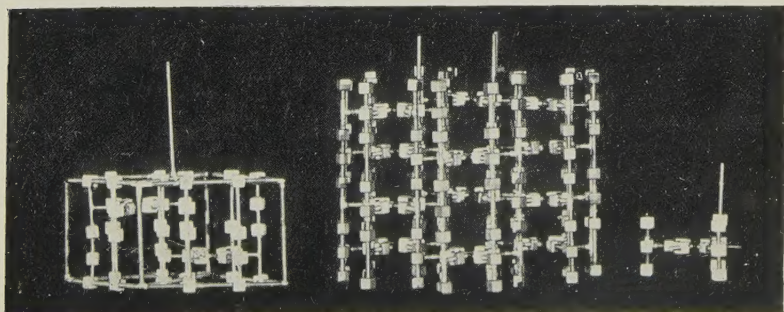
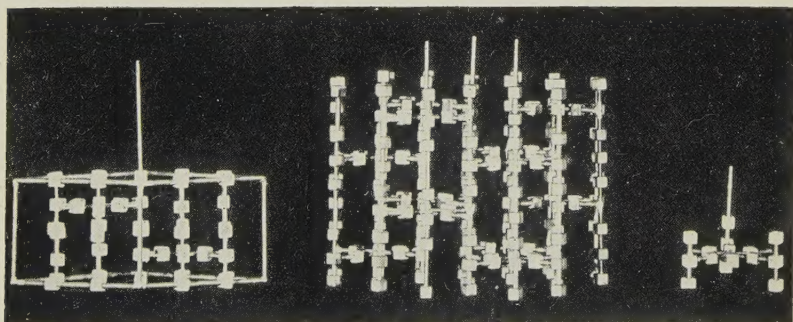
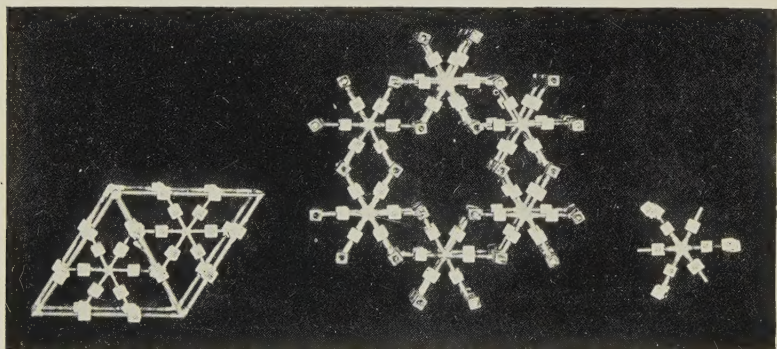
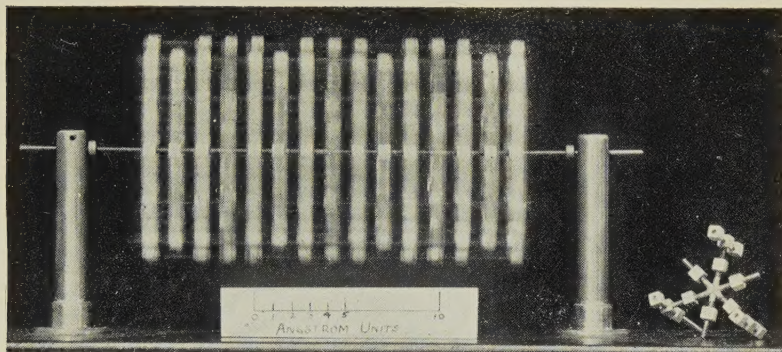
Most of the numerous diagrams are worthy of inclusion, but pictures of aeroplanes, whether modern or obsolete, and of some other familiar objects appear superfluous.

Frequent but concise biographical footnotes and examples from English University papers add to the usefulness.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



Diagrams 1-6.



(i.) Unit cell.

(ii.) Hexagonal model.

(iii) Molecule.

(Section 17, paras. 9-12.)

